

# High-Entropy Design of Lead-Free Halide and Oxide Semiconductors

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*“It gets easier. Every day it gets a little easier. But you gotta do it every day — that’s the hard part.”*

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## Kurzfassung

Die rasante Entwicklung von Perowskit-Solarzellen wurde durch die bemerkenswerten optoelektronischen Eigenschaften von Halogenid-Perowskiten auf Bleibasis vorangetrieben. Ihre breite kommerzielle Nutzung wird jedoch durch die Toxizität von Blei und die langfristige Umweltinstabilität erheblich behindert. Oxide-Halbleiter weisen zwar eine ausgezeichnete chemische und thermische Beständigkeit auf, haben jedoch noch keine wettbewerbsfähige Leistung in photovoltaischen Anwendungen erreicht. Diese Arbeit befasst sich mit diesen Herausforderungen, indem sie systematisch Materialien mit hoher Konfigurationsentropie als neuen Designansatz für nachhaltige, bleifreie Halbleitersysteme untersucht. Das ultimative Ziel ist die Entwicklung stabiler, lösungsverarbeitbarer Photovoltaik-Materialien. Diese Arbeit untersucht drei sich ergänzende Materialplattformen mit hoher Entropie: von Perowskit abgeleitete Halogenide, Perowskit-Oxide und Fluorit-artige Oxide. Jede Plattform ist für eine bestimmte Funktion innerhalb eines Photovoltaik-Gerätestapels ausgelegt.

Perowskit-abgeleitete Iodide mit hoher Entropie, basierend auf der  $\text{MA}_3\text{Bi}_2\text{I}_9$ -Struktur, wurden durch multikationische Substitution an der B-Stelle synthetisiert. Dieser Ansatz wurde genutzt, um ihre elektronischen Eigenschaften und ihre Defektlandschaft zu manipulieren. Die strukturelle, optische und photoelektronische Charakterisierung zeigte, dass die Einführung einer Variabilität der elementaren Konfiguration im Vergleich zur Ausgangsverbindung einstellbare Bandlücken, Veränderungen im defektbezogenen Emissionsverhalten und eine verbesserte Zusammensetzungsstabilität ermöglicht. Prototypische Photovoltaikvorrichtungen, die unter Verwendung dieser HEIs als Absorberschicht hergestellt wurden, unterstrichen die Bedeutung des Defektmanagements und der Grenzflächenoptimierung.

Auf dieser Grundlage wurden Perowskit-Oxide mit hoher Entropie als potenzielle Absorberlagen für vollständig anorganische, vollständig aus Oxiden bestehende Solarzellen entwickelt. Diese phasenreinen Mehrkomponentenoxide auf  $\text{LaBO}_3$ -Basis wurden mit einer skalierbaren lösungsbasierten Technik synthetisiert, die für die Dünnschichtabscheidung übertragen werden kann. Umfassende Untersuchungen ihrer kristallographischen, Schwingungs-, optischen und elektronischen Eigenschaften zeigen, dass sowohl die Bandstruktur als auch die Ionisationspotenziale durch die Beeinflussung der Zusammensetzung systematisch angepasst werden können. Obwohl die Umsetzung in Bauelementen noch in den Anfängen steckt, etablieren diese Ergebnisse hochentropische Perowskitoxide als vielversprechende und bisher unerforschte Plattform für Absorbermaterialien.

Um die Materialforschung über herkömmliche Trial-and-Error-Ansätze hinaus zu beschleunigen, wurde eine robotergestützte Lösungsverarbeitungsplattform in

Kombination mit automatisierter struktureller und optoelektronischer Charakterisierung eingesetzt, um eine hochdurchsatzfähige Synthese und ein Screening von hochentropischen Fluorit-Oxiden auf  $\text{CeO}_2$ -Basis durchzuführen. Diese Strategie ermöglichte eine schnelle Kartierung der Beziehungen zwischen Zusammensetzung, Struktur und Eigenschaften über einen breiten Zusammensetzungsbereich. Mehrere Zusammensetzungen wiesen günstige Bandausrichtungen, optische Transparenz und halbleitendes Verhalten auf, wodurch sie sich für die Anwendung als Elektronentransportschichten eignen.

Insgesamt zeigen die Ergebnisse dieser Arbeit, dass die Konfigurationsentropie einen leistungsstarken und universellen Designparameter für die Abstimmung der optoelektronischen Eigenschaften von Halbleitermaterialien darstellt. Die Arbeit etabliert Halogenide und Oxide mit hoher Entropie als umweltfreundliche Alternativen zu herkömmlichen photovoltaischen Materialien und bietet einen skalierbaren experimentellen Rahmen für die beschleunigte Entdeckung dieser Materialien. Obwohl weitere Optimierungen erforderlich sind, um industriell wettbewerbsfähige Wirkungsgrade zu erreichen, bietet der hier vorgestellte Ansatz mit hoher Entropie einen grundlegend neuen Weg zu stabilen, bleifreien Photovoltaik-Technologien und optoelektronischen Bauelementen der nächsten Generation.

## Abstract

Lead-halide-based perovskites have been the catalyst for the rapid advancement in the field of perovskite solar cells. Their remarkable optoelectronic properties come at the cost of lead toxicity and extreme sensitivity to environmental degradation, hindering their commercial scalability. Meanwhile, oxide semiconductors have demonstrated excellent chemical and thermal stability but have yet to achieve competitive performance in photovoltaic applications. This work addresses these challenges by systematically exploring high-entropy materials as a new design approach for sustainable, lead-free semiconducting systems. The ultimate goal is to develop stable, solution-processable photovoltaic device stacks. This work investigates three complementary high-entropy material platforms: perovskite-derived halides, perovskite oxides, and fluorite-type oxides. Each platform is designed for a specific function within a photovoltaic device stack.

High-entropy perovskite-derived iodides, based on the  $\text{MA}_3\text{Bi}_2\text{I}_9$  structure, were synthesised by multi-cationic substitution at the B-site. This approach was utilised to engineer their electronic properties and defect landscape. Structural, optical, and photoelectronic characterisation demonstrated that introducing configurational disorder allows for tunable band gaps, changes in defect-related emission behaviour, and enhanced compositional stability compared to the parent compound. Prototype photovoltaic devices made using these HEIs as the absorber layer emphasised the importance of defect management and interface optimisation.

Building on this, high-entropy perovskite oxides have been developed as potential absorber layers for fully inorganic, all-oxide solar cells. These phase-pure multicomponent oxides, based on  $\text{LaBO}_3$ , were synthesised using a scalable solution-based technique that can be transferred to thin-film deposition. Comprehensive investigations into their crystallographic, vibrational, optical, and electronic properties reveal that both the band structure and ionisation potentials can be systematically tailored through compositional engineering. Although device implementation is still in its early stages, these results establish high-entropy oxide perovskites as a promising and previously unexplored platform for absorber materials.

To accelerate materials discovery beyond conventional trial-and-error approaches, high-throughput synthesis and screening of  $\text{CeO}_2$ -based high-entropy fluorite oxides were performed using a robotic solution-processing platform, combined with automated structural and optoelectronic characterisation. This strategy enabled rapid mapping of composition–structure–property relationships across a broad compositional space. Several compositions exhibited favourable band alignments, optical transparency, and semiconducting behaviour, making them suitable for application as electron transport layers.

## Abstract

Collectively, the results of this thesis demonstrate that configurational entropy represents a powerful and universal design parameter for tuning the optoelectronic properties of semiconducting materials. The work establishes high-entropy halides and oxides as environmentally benign alternatives to conventional photovoltaic materials and provides a scalable experimental framework for accelerating their discovery. While further optimisation is required to reach industrially competitive efficiencies, the high-entropy approach introduced here offers a fundamentally new pathway toward stable, lead-free photovoltaic technologies and next-generation optoelectronic devices.

## Publications

### Publications in Peer-Reviewed Journals

- Kumbhakar, M.<sup>†</sup>, **Khandelwal, A.<sup>†</sup>**, Jha, S.K., Kante, M.V., Keßler, P., Lemmer, U., Hahn, H., Aghassi-Hagmann, J., Colsmann, A., Breitung, B., Velasco, L., and Schweidler, S. (2023), *High-Throughput Screening of High-Entropy Fluorite-Type Oxides as Potential Candidates for Photovoltaic Applications*. Adv. Energy Mater., 13: 2204337.

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<https://doi.org/10.1002/sml.202501703>

### Presentations at International Conferences

- *An insight into the functional properties of high-entropy perovskite oxides*, MRS Spring Meeting & Exhibit, 2024, Seattle, USA.

## Publications

- *High-throughput synthesis and characterisation of high-entropy oxides for photosensitive applications*, MRS Spring Meeting & Exhibit, 2023, San Francisco, USA.

## Posters at International Workshops

- *Sol-gel synthesis of high-entropy oxides for electrochemical applications*, NiPS-EnABLES Summer School, 2021, Perugia, Italy

## Awards

- Best Oral Presentation Award of the SF01 Symposium at MRS Spring Meeting & Exhibit 2023



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# 1 Introduction

## 1.1 Motivation

Fossil fuels have been the cornerstone of humanity's rapid progress over the past few centuries, providing easily accessible energy to meet most of humanity's demands. However, they come at the expense of worsening climate change, increased carbon emissions, and a host of geopolitical concerns. With the advent of artificial intelligence, machine learning, and computationally intensive technologies, energy requirements continue to increase. These challenges have intensified the global effort to reduce dependence on fossil fuels and accelerate the transition toward sustainable energy systems, as reflected by initiatives such as the Paris Agreement. Solar power plays a central role in this transition, owing to its vast availability and sustainability.

Photovoltaic cells (or solar cells), devices which convert sunlight into electrical energy using the photovoltaic effect, are at the heart of this transition. While silicon has been the industry standard for decades, there is a continuous search for new materials with improved efficiencies and lower associated costs. Perovskite solar cells are now at the forefront of solar cell research, promising higher efficiencies exceeding 26% with lab-scale devices and lower production costs due to simple, low-temperature processing using abundant, inexpensive raw materials. They can also be used for thin, lightweight, and flexible films, opening up possibilities for portable and integrated photovoltaic systems. However, they face two major hurdles to widespread commercialisation: lead toxicity and long-term stability. The most efficient perovskite solar cells use lead-based compounds, which can leach from damaged or discarded solar panels. Their high toxicity poses significant environmental and health concerns, as they contaminate soil and drinking water. Perovskite solar cells are also notoriously unstable, degrading when exposed to moisture, oxygen, heat, and even light. This considerably reduces their operational lifetimes, reducing their viability for commercialisation.

These concerns have now fuelled a search for lead-free perovskite alternatives that can achieve similar performances. Tin-based perovskites are the obvious choice for replacement due to their shared favourable electronic properties; however,  $\text{Sn}^{2+}$  oxidises to  $\text{Sn}^{4+}$ , creating defects in the crystal structure and reducing cell performance. Other perovskite derivatives, including those using bismuth and antimony, have also been investigated. Devices made from these halides have achieved a maximum efficiency of 4%, leaving room for further improvements. Ultimately, the goal is to develop a new generation of solar cells that are not only highly efficient and low-cost but also environmentally benign.

Oxide-based semiconductors offer another avenue for developing lead-free alternatives for solar cells. Oxides possess inherent structural stability against environmental

degradation, which is vital in increasing device lifetimes, and exhibit low toxicity. The ongoing research into perovskite solar cells, and particularly the quest for lead-free alternatives, represents a critical step towards a truly sustainable energy future. The successful development of this technology could revolutionise the solar industry and play a pivotal role in the global transition to clean energy.

### 1.2 Aim of the Work

The central aim of this thesis is to contribute to the development of sustainable, lead-free photovoltaic materials and to progress toward a fully solution-processable, all-oxide solar cell. This is to be achieved through the exploration of high-entropy materials, which exploit their configurational disorder to unlock functionalities not accessible in conventional low-component systems. It is also necessary to examine to what extent properties can be tailored in such systems using the high-entropy approach.

Prior to this work, no published studies had explored the impact of introducing compositional complexity to organometallic halides for photovoltaic applications. The work begins with the synthesis and evaluation of lead-free perovskite derivatives based on  $\text{MA}_3\text{Bi}_2\text{I}_9$  as novel absorber materials, alongside the design of a functional device architecture to assess their photovoltaic performance.

Building on this foundation, this thesis aims to further develop high-entropy perovskite oxides, moving towards an all-oxide solar cell stack. These materials are designed to exhibit favourable optoelectronic properties and to be compatible with synthesis routes that can be used to process them into thin films suitable for solar cell integration.

Finally, high-throughput combinatorial methods are employed to help expand the compositional space, which can be screened for high-entropy systems. A robotic synthesis setup, along with automated characterisation techniques, is utilised for rapid screening of  $\text{CeO}_2$ -based high-entropy rare-earth oxides as alternatives to  $\text{TiO}_2$  electron transport layers.



## 2 Scientific Background

### 2.1 High-Entropy Materials

High-entropy materials (HEMs) have gained prominence since the discovery of high-entropy alloys (HEAs) by Cantor and Yeh in 2004.<sup>[1,2]</sup> As both researchers reported these new systems independently and employed different terms for their findings, it has resulted in a perplexing array of terminology, such as entropy-stabilised materials, compositionally complex systems, and multi-principal element systems, to refer to such materials. Cantor referred to them as ‘equiatomic multicomponent alloys’, based on the alloy system comprising various elements in an equiatomic ratio.<sup>[1]</sup> Yeh, however, designated them as high-entropy alloys, positing that having more principal elements in the alloy system would facilitate the formation of a solid solution due to the high entropy of mixing.<sup>[2]</sup> As a result, “high-entropy” is now the prevailing descriptor for multicomponent systems.

Yeh designed his alloy system based on the relationship between system complexity and entropy given by the Boltzmann equation.<sup>[3]</sup>

$$S_{config} = -R \left( \sum_{i=1}^n x_i \ln x_i \right) \quad (1)$$

In Equation (1),  $S_{config}$  is the total molar configurational entropy,  $R$  is the universal gas constant,  $x_i$  represents the molar fraction of the constituent elements, and  $n$  is the number of constituent elements. Empirically, this quantity would reach its maximum value when the molar fractions for all constituents are equal, i.e.,  $x_1 = x_2 = \dots x_n$ . This behaviour can also be observed by plotting  $S_{config}$  as a function of the molar fraction of the constituent elements. Figure 1 illustrates the concept of the increasing configurational entropy with the addition of more constituent elements, and that the maximum value is obtained at equiatomic ratios of the constituents. For equiatomic systems with  $n$  constituent elements, Equation (2) now simplifies to

$$S_{config} = -R \left( \frac{1}{n} \ln \frac{1}{n} + \frac{1}{n} \ln \frac{1}{n} + \frac{1}{n} \ln \frac{1}{n} \dots + \frac{1}{n} \ln \frac{1}{n} \right) = -R \ln \frac{1}{n} = R \ln n \quad (2)$$

Thus, a five-component system would have a maximum  $S_{config}$  of  $1.61R$ , which was taken as the defining value for high-entropy systems.<sup>[4]</sup> However, this definition excluded systems with near-equiatomic compositions. Following this, a new classification system was established:



High-entropy:  $S_{config} \geq 1.5R$

Medium-entropy:  $1R \leq S_{config} < 1.5R$

Low-entropy:  $S_{config} < 1R$

This classification now includes compositions in which the individual elements have molar fractions between 0.05 and 0.35, which were previously excluded from the definition. This is now also the widely accepted nomenclature for high-entropy systems.<sup>[5,6]</sup>

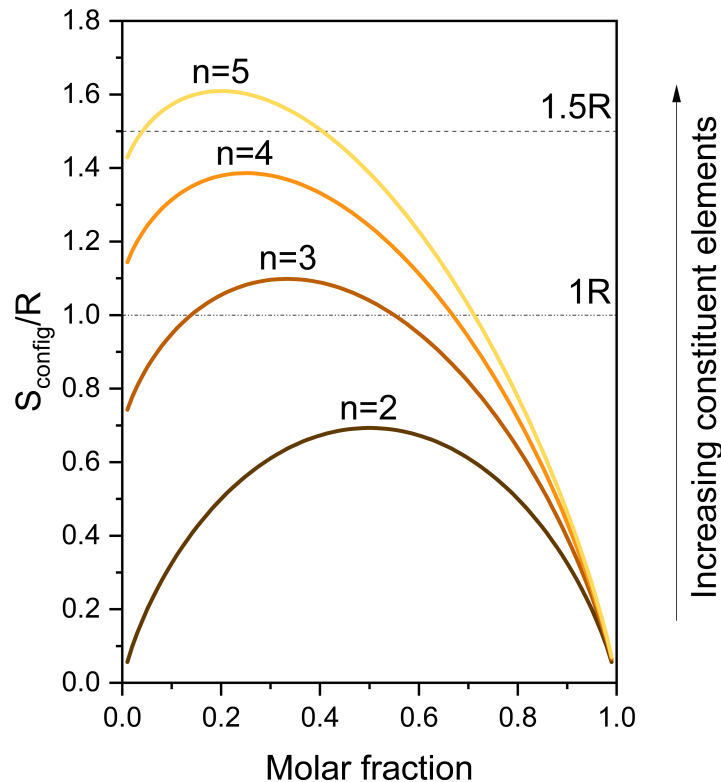


Figure 1: Dependence of the configurational entropy of an  $n$ -component system on the molar fraction of the  $n^{\text{th}}$  component.

## 2.1.1 Four Core Effects

Due to the complex nature of HEMs, a wide variety of factors can affect their properties. Yeh put forward four basic effects: high-entropy, severe lattice distortion, ‘sluggish diffusion’ and ‘cocktail’ effects, which could explain the idiosyncratic behaviour of HEMs.<sup>[4]</sup> These hypothesised effects are not necessarily present in all HEMs, but still help understand their behaviour.

### 2.1.1.1 High-Entropy Effect

This is considered the most important of the basic effects, giving these systems their name. The increased  $S_{config}$  in HEMs was credited for the crystallisation of a single-phase solid solution. This deviation is a departure from the norm as described by the Gibbs phase rule.<sup>[7]</sup>

$$P = C - F + 1 \quad (3)$$

In Equation (3),  $P$  is the maximum number of phases that can be formed,  $C$  is the number of components, and  $F$  corresponds to the degrees of freedom. For an  $n$ -component system at equilibrium, the value of  $P$  is  $n + 1$ . This means that as the number of elements increases, the likelihood of a multi-phase mixture increases. This is in stark contrast to HEMs, which crystallise in a solid solution with many fewer phases than predicted by the rule.

This behaviour can be attributed to the effect of the increased  $S_{config}$  on the Gibbs free energy ( $\Delta G_{mix}$ ), given by Equation (4).

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (4)$$

Here,  $\Delta H_{mix}$  and  $\Delta S_{mix}$  are the enthalpy and entropy of mixing at a given temperature  $T$  (in K). For the spontaneous formation of a phase, i.e., it is stable,  $\Delta G_{mix}$  must be negative. It is apparent that for  $\Delta H_{mix} = 0$  (an ideal solution) and  $\Delta H_{mix} < 0$ , the  $\Delta G_{mix}$  would be negative. However, for a non-ideal system,  $\Delta H_{mix}$  will be positive when the constituents do not harmonise together. Meanwhile,  $\Delta S_{mix}$  is always positive, making sure the term  $-T\Delta S_{mix}$  is always negative. Consequently, any enthalpic contributions can be overcome by having a high enough value for  $-T\Delta S_{mix}$ , resulting in a negative  $\Delta G_{mix}$  and a single phase. In HEMs, having a high  $S_{config}$  and a high synthesis temperature contributes to this large value of  $-T\Delta S_{mix}$ , resulting in the formation of a single-phase system. The thermodynamic stability of HEMs decreases with decreasing temperatures, making them metastable at room temperature.<sup>[6]</sup>

With the discovery of a large assortment of HEMs, it has been observed that having a high  $S_{config}$  (and  $\Delta S_{mix}$ ) does not necessarily result in the formation of a single phase. Conversely, not all so-called HEMs get their stability primarily from having a high  $S_{config}$ . Other entropic contributions,  $\Delta H_{mix}$ , and the synthesis temperature, also play a major role in determining the formation of HEMs.

#### 2.1.1.2 Severe Lattice Distortion Effects

HEMs contain a variety of elements within their lattice. Although these elements are selected to possess similar atomic radii and coordination, size disparities are anticipated. The random distribution of elements in the lattice results in variations in the local coordination and atomic sizes of these elements, leading to a distorted structure. This, in turn, impacts properties such as mechanical strength, electronic conductivity, and thermal conductivity.<sup>[8–12]</sup>

#### 2.1.1.3 ‘Sluggish Diffusion’ Effects

The chemical complexity of HEMs is also believed to hinder the diffusion processes within them. The local atomic environments define the diffusion in materials, as the local

bonds affect the energy at each site. Low-energy sites have a higher probability of trapping atoms in their minima, while high-energy sites create barriers to diffusion by forcing atoms to hop back to their original sites. The presence of either of these energy variances leads to slower diffusion rates. This behaviour is further exacerbated in HEMs due to the presence of a mixture of neighbouring cations and is often referred to as ‘*sluggish diffusion*’.<sup>[13]</sup> The metastability of HEMs at room temperature is frequently attributed to this sluggish diffusion of atoms, which prevents phase segregation during cooling. This may also influence other diffusion-controlled phenomena, such as grain growth and recrystallisation temperatures.

#### 2.1.1.4 ‘Cocktail’ Effects

Prof. Ranganathan proposed that the basic properties and synergistic effects of the constituent elements determine the properties of a system, and coined the term ‘*cocktail effects*’.<sup>[14]</sup> In HEMs, this is even more evident due to the increased mutual interactions among elements and severe lattice distortions. This results in the whole being greater than the sum of its parts, leading to unpredictable interactions and properties not observed in less complex systems. Since alterations in chemical composition can significantly affect the local chemical environment and oxidation state, HEMs create an expansive realm for tailoring and tuning properties. These ‘*cocktail effects*’ have become foundational for the development of HEMs with unique and targeted applications.

### 2.1.2 High-Entropy Oxides

High-entropy oxides (HEOs) are empirically classified as single-phase oxide systems with five or more cations randomly distributed across available lattice positions in an equiatomic (or near-equiatomic) ratio. The  $S_{config}$  for an  $A_xO_y$  type oxide can be calculated as:

$$S_{config} = -R \left( x \left( \sum_{i=1}^n x_i \ln x_i \right)_{A-site} + y \left( \sum_{j=1}^m y_j \ln y_j \right)_{O-site} \right) \quad (5)$$

Where,  $x_i$  and  $y_j$  are the molar fractions of the ions at the A-site and O-site (or anion site), respectively.  $n$  and  $m$  represent the number of cationic and anionic species at the A-site and O-site, respectively. In ideal situations (the absence of any oxygen vacancies and impurities), the value from the O-site on the  $S_{config}$  is zero. Therefore, the classification of HEOs is primarily based on the cationic composition of the system.

#### 2.1.2.1 Guidelines for Cationic Selection

Due to the immense possibilities available for forming HEOs, it is important to carefully select cations to ensure the synthesis of a single-phase system. The following criteria are often used and are based on Pauling’s rules for the crystallisation of ionic compounds.

1. The ionic sizes of the cations should be similar for a specific oxidation state and coordination number. This ensures lower probabilities of phase separation due to severe lattice mismatch. Moreover, in systems with multiple cationic sites present (like spinel or perovskite structures), the possibility of occupying different lattice positions should be considered.
2. There should exist at least one pair of the chosen mono-cationic oxides that do not exhibit complete miscibility and have a different crystal structure.

### 2.1.2.2 Entropy Stabilisation in HEOs

In 2015, Rost et al. synthesised a novel rock-salt structured HEO with the composition  $(\text{Co}_{0.2}\text{Cu}_{0.2}\text{Mg}_{0.2}\text{Ni}_{0.2}\text{Zn}_{0.2})\text{O}$ . During cyclic heat treatments between 750 °C and 1000 °C, they observed a reversible phase transformation between a single-phase and multi-phase solid solution. The single-phase HEO synthesised at 1000 °C would dissociate into a multi-phase solution at lower temperatures (less than 900 °C) and would be regained on subsequent reheating at higher temperatures.<sup>[15]</sup> This corroborated the previously theorised entropy stabilisation effect. Meanwhile, another HEO,  $(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_{2-\delta}$ , was discovered, which did not exhibit any phase separation even when heated at lower temperatures, i.e., its phase stability was not entropy-dependent. It was observed that cationic selection was a more dominant factor in its stability, as the removal of Ce from the system resulted in phase separation.<sup>[16]</sup> Since then, a large number of HEOs with various structures have been synthesised, such as perovskites,<sup>[17–21]</sup> fluorites,<sup>[22–26]</sup> rock-salt,<sup>[27,28]</sup> spinel,<sup>[29–31]</sup> pyrochlores,<sup>[32–34]</sup> rutile,<sup>[35]</sup> and layered,<sup>[36,37]</sup> which may or may not show entropy-driven phase stabilisation.

### 2.1.3 High-Entropy Perovskite Oxides

A large number of high-entropy perovskites (HEPOs) have already been reported, possessing properties remarkably distinct from conventional oxides, including enhanced catalytic activities, increased ferroelectric response, and higher chemical stability, among others. This has prompted the search for improvements in their optical and electronic characteristics as well. Liang et al. employed a sol-gel synthesis route to produce  $\text{Ba}(\text{Zr}_{0.2}\text{Sn}_{0.2}\text{Ti}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$  thin films with enhanced conductivities, and they were also able to control the band gap by varying the annealing temperature.<sup>[38]</sup> Reports on  $\text{Sm}^{3+}$ -doped  $\text{Ca}(\text{Zr}_{0.2}\text{Ti}_{0.2}\text{Sn}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2})\text{O}_3$  have shown that photoluminescent behaviour can be enhanced using the high-entropy concept.<sup>[39]</sup>

However, investigations into their opto-electronic properties and applications are still scarce. A-site substitutions in compositions like  $(\text{La}_x\text{K}_{0.4-x}\text{Ca}_{0.2}\text{Sr}_{0.2}\text{Ba}_{0.2})\text{TiO}_{3+\delta}$ ,  $(\text{Gd}_{0.2}\text{Nd}_{0.2}\text{La}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{CoO}_3$  and  $(\text{La}_{0.2}\text{Lu}_{0.2}\text{Y}_{0.2}\text{Gd}_{0.2}\text{Ce}_{0.2})\text{AlO}_3$  have indicated that optical properties like reflectivity, photoluminescence and band-gap can be finely tuned in HEPOs.<sup>[40–43]</sup> Control of the optoelectronic properties through B-site changes is yet to be studied in detail.

## 2.1.4 High-Entropy Fluorite-Structured Oxides

Fluorite-structured oxides have been widely utilised in solid oxide fuel cells (SOFCs), catalysts, thermal barrier coatings, and other applications, due to their high ionic conductivity and chemical stability, among other attractive properties.<sup>[44–48]</sup> The most popular compositions involve  $\text{CeO}_2$  and  $\text{ZrO}_2$ . As the fluorite structure involves cations accommodating the 8-fold coordination of oxygen, as seen in Figure 2, 4+ cations are required. As the  $\text{Zr}^{4+}$  cation is smaller, it is often doped with larger cations, such as  $\text{Y}^{3+}$ , to stabilise the fluorite structure. This prerequisite of doping within fluorite structures enables increased control over their ionic conductivities and band gaps. The presence of oxygen vacancies within these systems also enables inherent n-type semiconductivity in some cases.<sup>[49]</sup>

Upon the discovery of the first high-entropy fluorite-structured oxide,  $(\text{Ce}_{0.2}\text{La}_{0.2}\text{Pr}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2})\text{O}_2$ , multitudes of reports on various other compositions have been published.<sup>[16]</sup> Subsequent studies revealed that the band gap can be extensively tuned, varying from 2 eV to more than 5 eV, by changing the composition.<sup>[50–52]</sup> Most further reports have mainly focused on their ionic conduction for SOFC applications and thermal response.<sup>[23,26,53–56]</sup> Spiridigliozzi et al. also developed a model based on the standard deviation of the cationic radii of selected elements to predict the formation of fluorite-structured oxides. For systems with deviations greater than 0.095, a fluorite structure is expected, whereas values below 0.095 lead to either a biphasic fluorite-bixbyite mixture or a purely bixbyite phase.<sup>[57]</sup>

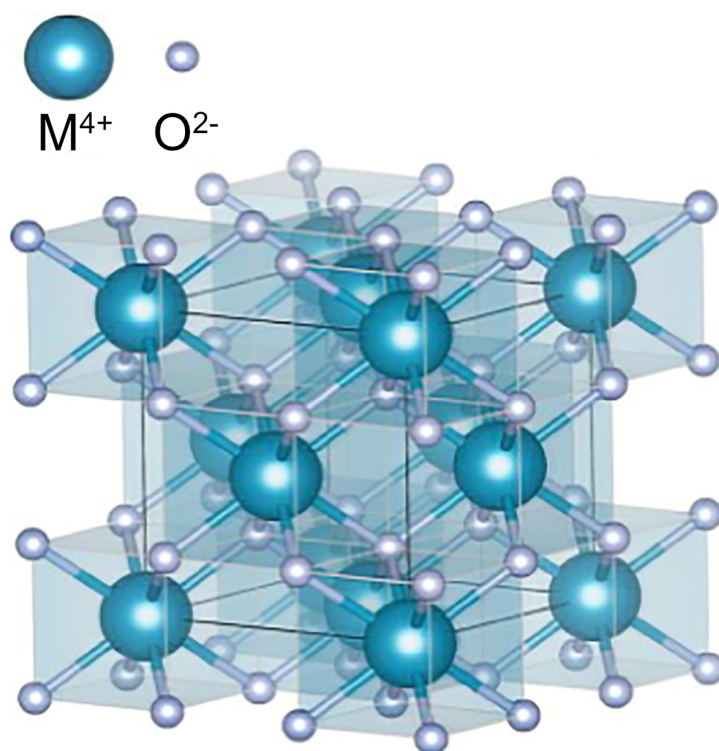


Figure 2: Typical structure of a fluorite-structured oxide<sup>[58]</sup>. Figure published under license CC BY 4.0.

## 2.1.5 High-Entropy Halides

High-entropy halides are a relatively unexplored class of HEMs. There have been a few reports on the development of high-entropy chlorides and bromides as electrolytes for solid-state batteries, as well as fluorides for use in conversion-based batteries. However, halides have immense unexplored potential in applications such as catalysis, photovoltaics, and other semiconductor devices. In particular, halide perovskites are currently the most effective materials in their class for use as absorbers in solar cells. Thus, the development of a stable lead-free absorber is a very exciting foray.

The majority of reports on high-entropy halides have primarily focused on the development of double perovskite chlorides for solid-state batteries.<sup>[59–62]</sup> Solari et al. successfully retained excellent optical properties by reducing the Pb content in MAPbBr<sub>3</sub>-based perovskites through the introduction of Mg, Zn, and Cd at the B-site. The use of Cd in this system, although not ideal, is promising for understanding the behaviour of multi-cationic halide perovskites.<sup>[63]</sup>

So far, there has been one report on a high-entropy iodide, where the authors reported a reduction in the degradation rate of GA<sub>x</sub>FA<sub>x</sub>EA<sub>x</sub>AC<sub>x</sub>MA<sub>1–4x</sub>PbI<sub>3</sub> (GA – guanidinium, FA – formamidinium, EA – ethylammonium, AC – acetamidinium) compared to MAPbI<sub>3</sub>.<sup>[64]</sup> Another report by Song et al. showed increased stability in humid conditions for (CHA)<sub>2</sub>PbBr<sub>4</sub> (CHA – cyclohexylamine), which had various substitutions at all sites of the perovskite structure.<sup>[65]</sup> This represents a promising basis for further development of this material class.

## 2.2 Introduction to Perovskites

Perovskite materials, named after the mineral calcium titanate (CaTiO<sub>3</sub>), share a general formula of ABX<sub>3</sub>, where A is the larger cation, B is the smaller cation, and X is an anion. Perovskites have garnered significant attention for their diverse applications, which include photovoltaics,<sup>[66–68]</sup> catalysts,<sup>[69,70]</sup> sensors,<sup>[71–73]</sup> superconductors,<sup>[74]</sup> and more. Perovskites can accommodate a wide variety of elements, enabling substantial tuning of their optical,<sup>[75,76]</sup> electronic,<sup>[77,78]</sup> and magnetic properties.<sup>[18,79]</sup> As interest in these materials grew, it was also observed that multiple cations with varying oxidation states could be accommodated within the same structure. This led to the discovery of more complex materials with promising properties, such as A<sub>2</sub>BB'X<sub>6</sub> and A<sub>3</sub>B<sub>2</sub>B'X<sub>9</sub>, all of which belong to the perovskite family.<sup>[80–82]</sup>

### 2.2.1 Structural Properties of Perovskites

Perovskites possess a cuboctahedral structure, with the A-site located at the centre of a cuboctahedron, surrounded by corner-sharing BX<sub>6</sub> octahedra,<sup>[83]</sup> as illustrated in Figure 3. In halide perovskites, the A-site is typically occupied by methylammonium (MA<sup>+</sup>), formamidinium (FA<sup>+</sup>), caesium (Cs<sup>+</sup>), among others; the B-site is filled by lead (Pb<sup>2+</sup>),



while the anion consists of iodide ( $I^-$ ), bromide ( $Br^-$ ), and chloride ( $Cl^-$ ). In oxide perovskites, the A-site may include lanthanum ( $La^{3+}$ ) and barium ( $Ba^{2+}$ ), as examples. The B-site is filled by cations that complement the A-site, such as chromium ( $Cr^{3+}$ ), manganese ( $Mn^{3+}$ ), or titanium ( $Ti^{4+}$ ), to maintain charge neutrality. The anion in this scenario is oxygen ( $O^{2-}$ ). The stability of a perovskite structure can be assessed using two geometrical parameters, the Goldschmidt tolerance factor ( $t$ )<sup>[84]</sup> and the octahedral factor ( $\mu$ )<sup>[85]</sup> which are defined by Equations (6) and (7), respectively.

$$t = \frac{r_A + r_B}{\sqrt{2}(r_B + r_X)} \quad (6)$$

$$\mu = \frac{r_B}{r_X} \quad (7)$$

Here,  $r_A$ ,  $r_B$ , and  $r_X$  represent the ionic radii for the A-site, B-site, and X-site ions, respectively. The Goldschmidt tolerance factor describes how well the A-site cation can fit in the voids of the corner-sharing  $BX_6$  octahedra, i.e. the stability of the perovskite structure. When the cation fits perfectly in the void, for  $0.9 < t < 1$ , an ideal cubic structured perovskite is formed. For the range,  $0.7 < t < 0.9$ , a distorted perovskite structure, such as rhombohedral or octahedral, is possible. When  $t > 1$ , the A-site cation is too large for the void, resulting in low-dimensional perovskites or other non-perovskite structures due to the fragmentation of the octahedral layer. Finally, for  $t < 0.7$ , the cation is too small and forms unstable structures. On the other hand, the octahedral factor quantifies the fit of the B-site cation at the centre of the octahedron formed by the anions, i.e., the distortion of the  $BX_6$  octahedra. When this factor is in the range of  $0.414 \leq \mu \leq 0.732$ , a stable  $BX_6$  octahedron can be formed. When the value of  $\mu < 0.414$  or  $\mu > 0.732$ , the B-site cation is too small or too large, respectively, to create a stable octahedra.<sup>[86–88]</sup>

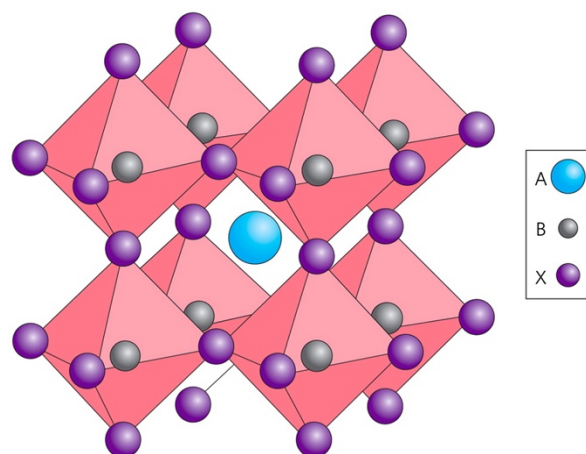


Figure 3: Crystal structure of a typical perovskite structure<sup>[89]</sup>. Reproduced with permission from Springer Nature.

Bartel et al. reported a new tolerance factor  $\tau$ , which helps further improve the stability prediction for perovskite structures by including the influence of the oxidation state of the A-site cation<sup>[90]</sup>. The value  $\tau$  is calculated by Equation (8).

$$\tau = \frac{r_X}{r_B} - n_A \left( n_A - \frac{r_A/r_B}{\ln r_A/r_B} \right) \quad (8)$$

Here,  $n_A$  refers to the oxidation state of the A-site cation.  $\tau < 4.18$  suggests that a perovskite structure is possible.

## 2.2.2 Perovskite Derivatives

Although lead-based perovskites have been extensively studied, resulting in perovskite solar cells (PSCs) with power conversion efficiencies (PCE) exceeding 25%, further improvement and commercialisation are hampered by the toxicity and poor environmental stability of lead.  $\text{Pb}^{2+}$  is easily oxidised to  $\text{Pb}^{4+}$ , thus requiring extensive encapsulation techniques to prevent material degradation.<sup>[91]</sup> The search for lead-free perovskites resulted in the discovery of various perovskite-adjacent structures due to the deviation in the oxidation states of constituent elements, as shown in Figure 4.

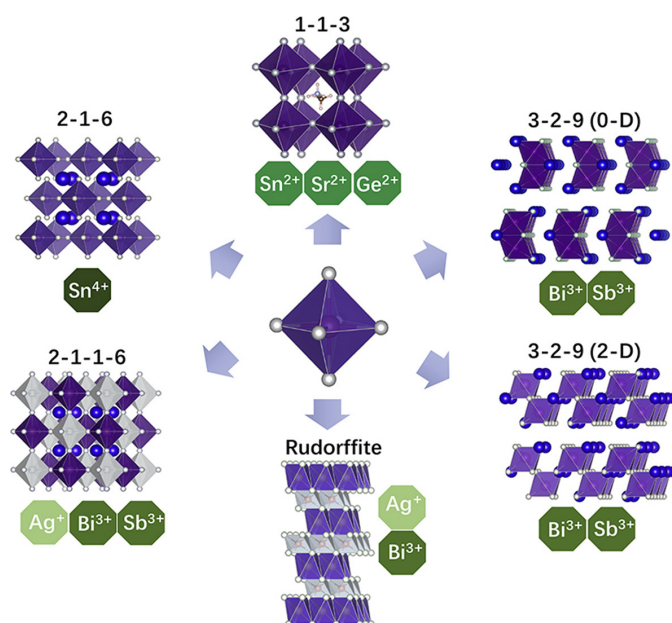


Figure 4: Illustrations of various perovskite-derived structures<sup>[92]</sup>. Reproduced with permission from Elsevier.

The exceptional optoelectronic properties of Pb-based perovskites are primarily due to the optimal electronic configuration of  $\text{Pb}^{2+}$ .<sup>[93,94]</sup> Bi- and Sb-based materials were considered promising alternatives, owing to their lower toxicity and higher chemical stability.  $\text{Bi}^{3+}$  has a similar ionic radius, electronic configuration, and electronegativity to  $\text{Pb}^{2+}$ , so it demonstrates potential as a substitute for lead. This led to the discovery of  $\text{A}_3\text{Bi}_2\text{X}_9$  triple-perovskite derivatives with band gaps near 2 eV. These emerging  $\text{A}_3\text{Bi}_2\text{X}_9$  structured materials exhibit reduced dimensionality (0D or 2D) compared to the  $\text{ABX}_3$



perovskites, leading to greater stability against degradation.<sup>[95]</sup> However, their performance has been restricted by heavier carrier effective masses, wider band gaps, and higher exciton binding energies.  $\text{MA}_3\text{Bi}_2\text{I}_9$  is the most popularly studied polymorph from this class of materials. It comprises two face-sharing  $[\text{BiI}_6]$  octahedra, forming a 0D dimer. A maximum PCE of 3.17% has been achieved for  $\text{MA}_3\text{Bi}_2\text{I}_9$  with long-term stability, marking a significant improvement from the original discovery of 0.12% PCE in 2015.<sup>[96,97]</sup> Theoretical modelling of  $\text{Sb}^{3+}$ -based PSCs suggests that a stable PCE of 23.10% is possible<sup>[98]</sup> by optimising defect densities and layer thickness. Other substitutions include combinations of cations, such as  $\text{Ag}^+$ ,  $\text{Na}^+$ , and  $\text{In}^{3+}$ , to form double perovskites or other derivatives.<sup>[99]</sup> Most efforts focus on tuning the B-site cations to minimize the influence of toxic elements, controlling trap-state densities, and passivating grain boundaries to enhance device performance.

### 2.2.3 Working Principles of PSCs

PSCs employ several key steps, facilitated by the different layers within the cell structure, to generate electrical power. These are illustrated in Figure 5(a).

#### 2.2.3.1 Light Absorption

The absorber layer of a PSC captures incident photons with energy more than its band gap, exciting electrons from the valence band to the conduction band. This generates bound electron-hole pairs (known as excitons) within the absorber layer.

#### 2.2.3.2 Exciton Separation

These excitons are then separated by the absorber layer into charge carriers (i.e. free electrons and holes) due to the internal potential of the cell.

#### 2.2.3.3 Charge Extraction

Free electrons are transported through the electron transport layer (ETL) to the negative electrode (cathode), while holes are carried to the positive electrode (anode) via the hole transport layer (HTL). ETLs are typically n-type semiconductors, such as titanium dioxide, and HTLs are generally p-type semiconductors, like Spiro-OMeTAD.

#### 2.2.3.4 Charge Collection

The charge-carriers are collected at the respective electrodes. Electrical current is produced by moving electrons to the anode through an external load.

It is essential to optimise the energy levels of the different layers of the cell to ensure the generation of charge carriers within it. Incorrect band alignments can result in the recombination of the charge carriers. Tuning the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the layer materials helps increase their viability for a successful cell stack.

## 2.2.4 Recombination Losses

Losses arising from charge-carrier recombination pose a significant obstacle to achieving high efficiencies with PSCs. Band-to-band recombination, shown in Figure 5(b), occurs due to direct electron-hole recombination without electron relaxation and Auger recombination in the case of indirect transitions, and is not significant in the case of most PSCs<sup>[100]</sup>. However, the presence of defects in the absorber layer results in trap-assisted recombination (also known as Shockley-Read-Hall) and promotes recombination at the absorber/transport layer interface, shown in Figure 5(c) and Figure 5(d). This presents a considerable challenge when employing oxide perovskites as the absorber layer due to the inherent oxygen vacancies and ionic defects, which create both deep and shallow trap states that facilitate these mechanisms.

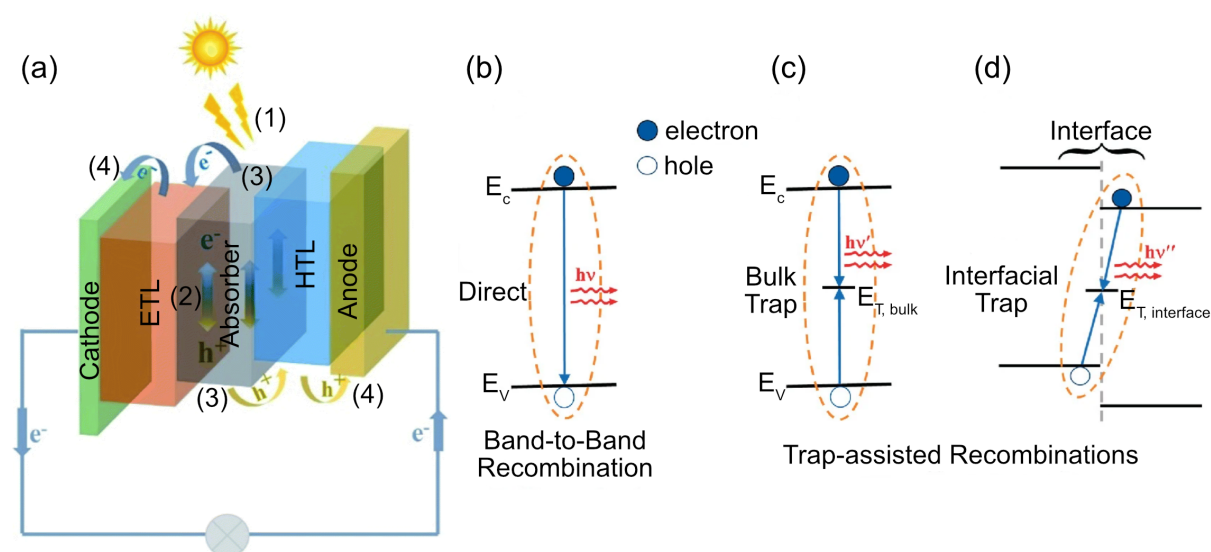


Figure 5: (a) Working principle of PSCs<sup>[101]</sup> (Reproduced with permission from the Royal Society of Chemistry); Pathways for recombination losses: (b) Band-to-band recombination within the absorber layer, (c) Trap-assisted recombination via bulk traps within the absorber layer, (d) Trap-assisted recombination via interfacial traps between the absorber layer and charge transport layers<sup>[102]</sup> (Reproduced with permission from Springer Nature).

## 2.3 High-Throughput Synthesis Techniques

The development of new materials is essential for enabling technological advances and has driven the exploration of increasingly complex material systems to meet demands for enhanced performance and more sophisticated functionalities. These innovations generally occur through incremental changes to the existing framework of synthesis techniques, parameters, and materials. As the compositional space available for synthesising HEMs encompasses multitudes of elements, optimising them necessitates identifying the optimal composition from millions of possibilities. Achieving this within the constraints of laboratory conditions is not feasible due to the complexity of data analysis and the numerous experiments involved. High-throughput techniques, combined with machine learning and theoretical models to predict properties, provide

an effective solution to this challenge. These approaches facilitate the development of extensive material libraries and yield valuable insights into their properties. Furthermore, the experimental data generated by these studies can be utilised to train machine learning and artificial intelligence models, thereby reducing the need for subsequent synthesis and characterisation and accelerating the pace of functional materials discovery.<sup>[103]</sup>

Inspired by the molecular libraries used by biologists to discover new drugs, Xiang et al. sought to utilise the same approach for unearthing new solid-state materials. They generated their libraries by combining thin-film sputtering with physical masks to control the elemental composition of samples as small as 200  $\mu\text{m}$  by 200  $\mu\text{m}$ , which they then tested for electrical properties.<sup>[104]</sup> Such combinatorial techniques were then combined with the high-entropy concept to synthesise and characterise high-entropy alloys.<sup>[105,106]</sup> Meanwhile, automated solution-dispensing robotic systems enabled the rapid exploration of large sample sets in much shorter durations through the use of liquid-phase precursors for coprecipitation and sol-gel synthesis routes.<sup>[107,108]</sup> Finally, the advent of automation within measurement techniques has helped in the growth of high-throughput characterisations. Now, materials libraries of HEMs can be created, and their composition-structure-performance relationships can be accurately mapped. Strotkötter et al. could screen the compositional space of sputtered  $(\text{CoCrFeMnNi})_3\text{O}_4$  for oxygen evolution reactions (OER) and successfully transfer the results to particles.<sup>[109]</sup> The mass transport properties and electrochemical performance of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Mn}_x\text{Co}_y\text{Fe}_z\text{O}_{3\pm\delta}$  perovskites were successfully predicted using machine learning methods by Bozal-Ginesta et al. for SOFC applications, with optimal compositions being delivered.<sup>[110]</sup> Other tasks, which typically require manual analysis, such as phase and parameter determination from X-ray diffraction (XRD), have also been successfully performed by neural networks that can be trained on material libraries created using high-throughput techniques.<sup>[111]</sup>



## 3 Experimental Methods

### 3.1 Characterisation Techniques

#### 3.1.1 X-Ray Diffraction

XRD is a widely used non-destructive technique for investigating the crystal structure of a material. X-rays have a wavelength in the range of 10 pm to 10 nm, out of which a small part, between 0.05 nm and 0.25 nm, is in the same order of magnitude as the interatomic distances in a crystal lattice and is usable for diffraction studies.<sup>[112]</sup> When X-rays are incident on a crystal, they undergo elastic scattering at the different lattice planes present within the crystal structure. This results in the diffracted beams undergoing constructive or destructive interference depending on their phase difference. The diffraction angles satisfying the conditions for constructive interference are governed by Bragg's law:<sup>[113]</sup>

$$2d \sin \theta = n\lambda \quad (9)$$

In Equation (9),  $d$  is the distance between lattice planes,  $\theta$  is the angle of diffraction,  $n$  is the order of reflection (always an integer), and  $\lambda$  is the wavelength of the incident X-rays.

We can see from Figure 6, the difference in the path length of the two parallel X-rays is  $2d \sin \theta$ . For constructive interference to occur, the diffracted beams must be in phase, i.e., an integer multiple of the X-ray wavelength. The constructive interference for diffraction from the atomic planes of a crystal structure can be detected from their increased signal intensities, which is the basis for XRD. This diffraction pattern is unique for all crystal structures and can be used to identify them. Using refinement techniques, such as Rietveld refinement, information like microstrain, average grain size, and texture can also be extracted from the XRD patterns.<sup>[115]</sup>

The diffraction techniques used for this thesis are:

##### 3.1.1.1 Powder XRD

Two devices were used to measure the XRD patterns for polycrystalline HEM powders. A D8 Advance (Bruker) diffractometer with a Cu-K $\alpha_{1,2}$  source, a Ni filter and a LynxEye 1D detector was used to measure samples in air. This device had a Bragg-Brentano geometry, where both the source and detector simultaneously move along the goniometer, focused on a fixed sample stage. The source and detector always move synchronously relative to the sample stage, thereby maintaining the same angle ( $\theta$ ) for the incident and detected radiations. A Stadi P (STOE) diffractometer, equipped with a Ga-jet X-ray source (Ga-K $\beta$  radiation, Å) and operating with a Bragg-Brentano geometry, was used to measure air-sensitive samples covered with Kapton foil. Rietveld refinements of the XRD patterns were performed using the Profex software.<sup>[116]</sup> The

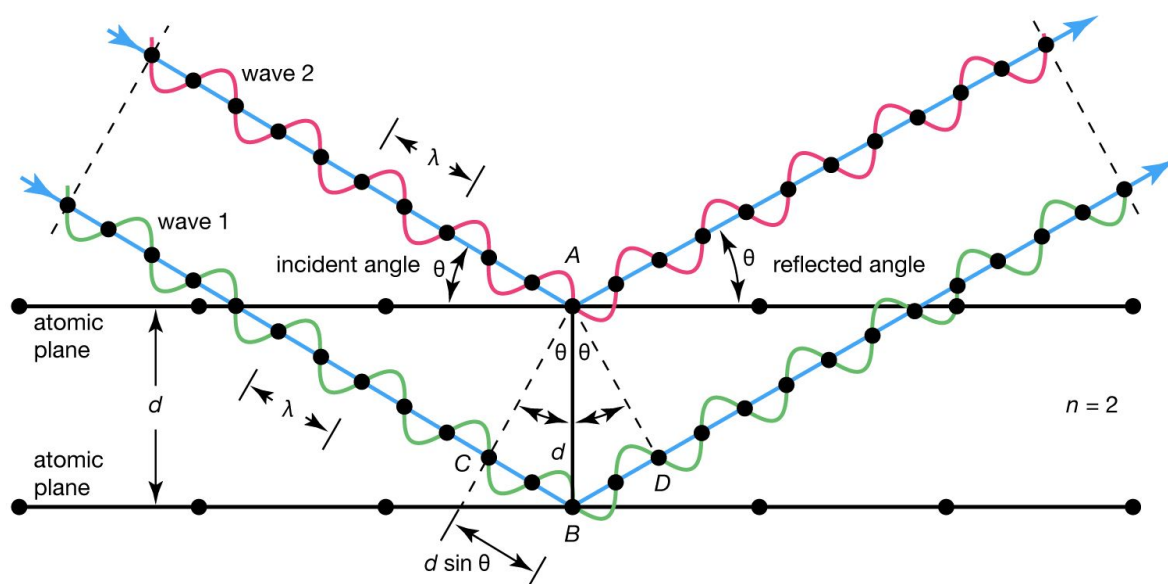
instrument parameters were obtained with the help of SRM-1976b (strain-free  $\text{Al}_2\text{O}_3$  in a glassy matrix with a particle size greater than  $2\text{ }\mu\text{m}$ ).

### 3.1.1.2 Automated XRD

Transmission XRD patterns were obtained using a Stadi P (STOE) diffractometer, equipped with a Ga-jet X-ray source (Ga- $\text{K}\alpha$  radiation,  $1.34\text{ }\text{\AA}$ ) and a custom-built XY stage for automated sample measurement. For all the samples, a semi-automated Le Bail Fit was done using Topas Academics V5 software.

### 3.1.1.3 Grazing Incidence XRD

This was used to investigate the structure of thin films in air using an Empyrean 3 (Malvern Panalytical) with a  $\text{Cu-}\text{K}\alpha_{1,2}$  source and PIXcel<sup>1D</sup> detector. Grazing incidence XRD operates at very small fixed  $\theta$  values ( $0^\circ - 5^\circ$ ), which satisfy the conditions of total internal reflection in the thin films. The detector moves along the goniometer around the sample (like powder XRD) to measure the diffraction pattern.



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*Figure 6: Bragg diffraction. Waves 1 and 2, in phase with each other, glance off atoms A and B of a crystal that has a separation distance  $d$  between its atomic, or lattice, planes. The reflected (glancing) angle  $\theta$ , as shown by experiment, is equal to the incident angle  $\theta$ . The condition for the two waves to stay in phase after both are reflected is that the path length  $CBD$  be a whole number ( $n$ ) of wavelengths ( $\lambda$ ), or  $n\lambda$ . But, from geometry,  $CB$  and  $BD$  are equal to each other and to the distance  $d$  times the sine of the reflected angle  $\theta$ , or  $d \sin \theta$ . Thus,  $n\lambda = 2d \sin \theta$ , which is the Bragg law. As may be seen from the diagram, when  $n = 2$ , there is only one wavelength along path  $CB$ ; also, the reflected angle will be smaller than that for, say,  $n = 3$ . Waves reflected through an angle corresponding to  $n = 1$  are said to be in the first order of reflection, the angle corresponding to  $n = 2$  is the second order, and so on. For any other angle (corresponding to fractional  $n$ ), the reflected waves will be out of phase, and destructive interference will occur, annihilating them.<sup>[114]</sup> Reproduced with permission from Encyclopædia Britannica, Inc.*

### 3.1.2 X-Ray Fluorescence

X-ray fluorescence (XRF) is a non-destructive analytical technique used to determine the elemental composition of a material through its interaction with X-rays. When a sample is irradiated with X-rays, some of the X-rays are absorbed, leading to various phenomena such as scattering and the release of photons, electrons, and fluorescent X-rays. XRF is a three-step process, as shown in Figure 7.

1. The primary X-ray ejects an electron after collision, from an orbital surrounding the nucleus within an atom of the material.
2. The resulting vacancy in the orbital leaves the atom in a high-energy, unstable configuration.
3. An electron from a higher energy level relaxes to fill this vacancy to restore equilibrium. Since the electron is falling to a lower energy level, it emits excess energy as fluorescent X-rays.

This emitted fluorescent X-ray is characteristic of the element from whose atom it originates, due to the unique energy levels associated with each element. The energy of the fluorescent X-rays is also independent of the chemistry of the materials.

An XGT-9000 micro-XRF analyser (HORIBA) was used for the analysis in this thesis.

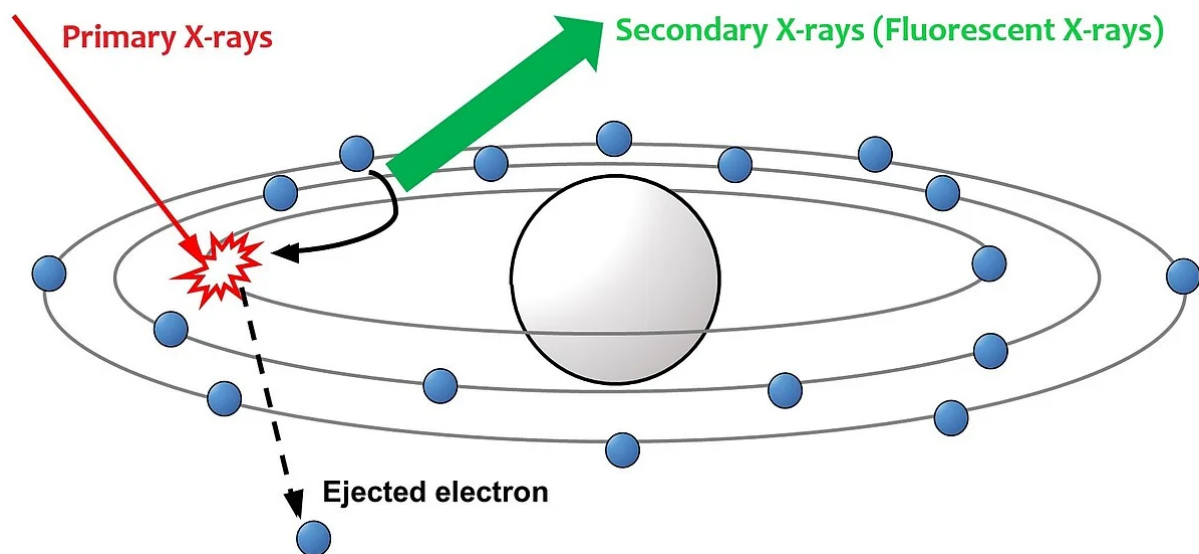


Figure 7: Principle of X-ray fluorescence.<sup>[117]</sup>

### 3.1.3 Scanning Electron Microscopy

An electron microscope functions similarly to an optical microscope, but it uses electrons instead of light for imaging. Due to the smaller wavelength of electrons compared to visible light, electron microscopes can achieve much higher magnification and better resolution than optical microscopes.<sup>[118]</sup> In a scanning electron microscope (SEM), a primary electron beam is emitted from an electron gun and then focused onto

the sample using electromagnetic lenses, as shown in Figure 8(c). The surface of the sample is scanned in a raster fashion using deflection coils, giving the technique its name. The interaction of the primary electron beam with the sample surface yields various types of energetic emissions, depending on the penetration depth, as illustrated in Figure 8(a). Figure 8(b) illustrates the mechanism for producing the three major emissions utilised in SEM imaging.

### *3.1.3.1 Secondary Electrons (SE)*

The inelastic scattering of primary electrons from the surface or near-surface region of the sample results in the emission of secondary electrons. As primary electrons lose energy through interactions with sample atoms, only those with shallow penetration depths can escape. Therefore, these give information about the surface morphology of the sample. They are measured by a detector with a bias voltage placed at the side of the electron chamber, often at an angle to increase the efficacy of electron capture.

### *3.1.3.2 Back-Scattered Electrons (BSE)*

These originate from the elastic scattering of the primary beam after interactions with a broad region of the sample atoms. Due to the lower energy loss from the elastic scattering, they can surface from deeper depths. As larger atoms can more strongly scatter the incident electrons, the signal intensities of back-scattered electrons are proportional to the atomic number of the atoms. This dependence on the atomic number helps provide contrast between different phases while imaging. BSE detectors are placed in a concentric ring around the primary electron beam to boost their collection efficiency.

### *3.1.3.3 Characteristic X-Rays*

These are emitted when an electron moves from an outer shell to an inner-shell vacancy created by the expulsion of an inner-shell electron due to the inelastic scattering of the primary beam. Since ionisation energies are unique to the different shells of each element, each relaxation has a characteristic energy. These characteristic X-rays can be used to analyse the elemental composition and distribution within the sample, and the technique is called energy-dispersive X-ray spectroscopy (EDS). Lighter elements (atomic numbers smaller than 10) cannot be accurately measured using EDS. EDS and XRF differ from each other in a few key ways:

1. Characteristic X-rays are emitted due to the interaction of high-energy electrons with the sample in EDS, while inner-shell electrons are excited by high-energy X-rays in the case of XRF.
2. EDS has high spatial resolution and is great for elemental mapping, while XRF provides information averaged over the bulk.
3. XRF is more sensitive and has lower detection limits than EDS, even helping detect lighter elements.



Apart from the aforementioned emissions, there are others, including Auger electrons, cathodoluminescence, and continuum X-rays. However, these will not be delved into for the scope of this thesis. It is also crucial that the sample is conducting to prevent charge accumulation at the surface while imaging. A thin layer ( $\sim 10$  nm) of a conducting material, such as gold, can be sputtered onto the surface of non-conductive samples to ensure proper imaging.

A LEO Gemini-1530 (Carl Zeiss AG) scanning electron microscope equipped with an Oxford X-Max<sup>N</sup> X-ray detector was used for SEM imaging in this thesis.

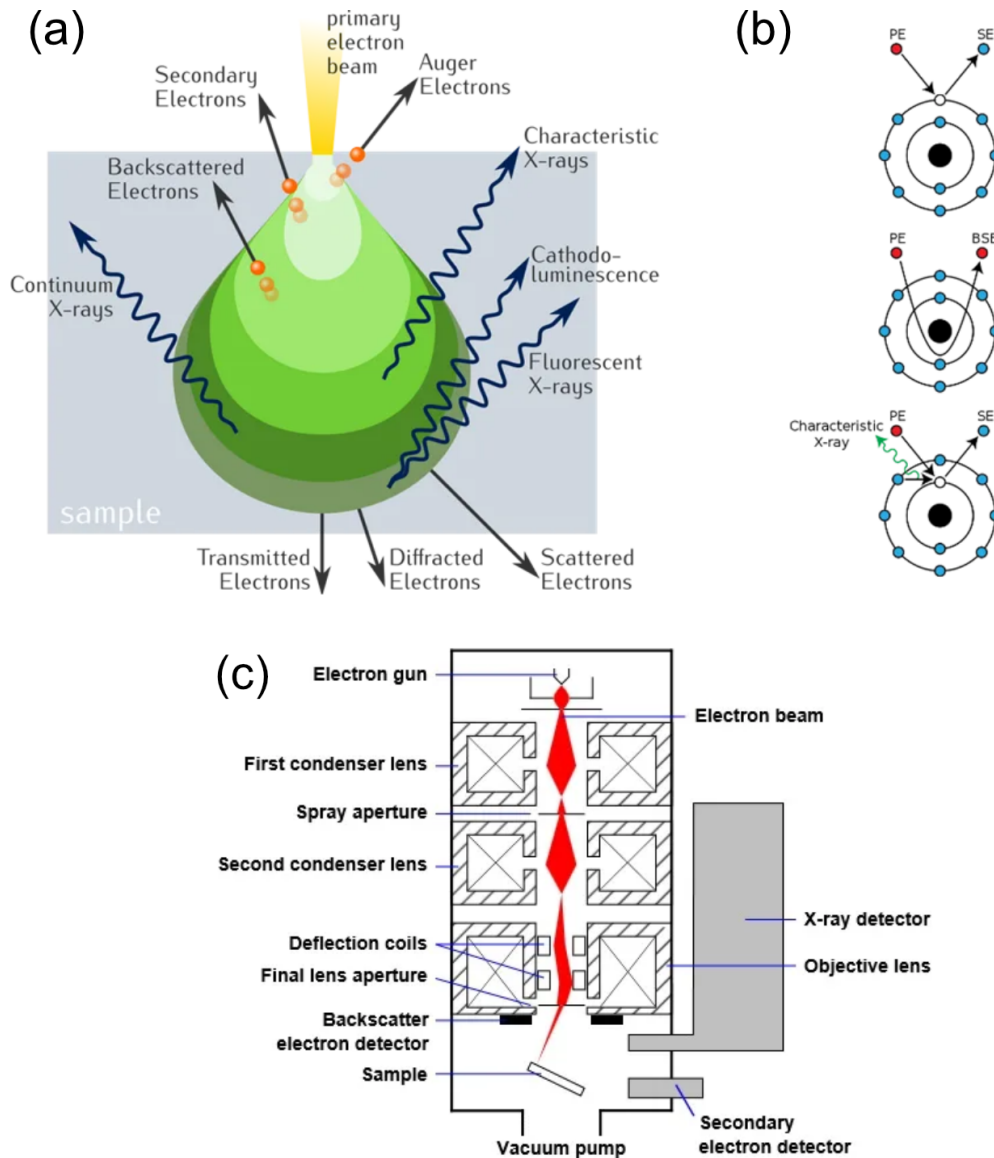


Figure 8: (a) Different interactions between the incident electron beam and the sample, (b) Illustrations for the emission of secondary electron, back-scattered electron, and characteristic X-ray after the scattering of the primary electron, and (c) a schematic view of the components of an SEM.<sup>[119]</sup>

### 3.1.4 Ultraviolet-Visible-Near Infrared Absorption Spectroscopy

Ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy is a characterisation technique used for investigating the optical absorption spectra of a material. The absorbance of a material ( $A$ ) is quantified as the ratio of the incident radiation intensity ( $P_\lambda^0$ ) to the transmitted radiation intensity ( $P_\lambda$ ), Equation (10).

$$A = \log_{10} \frac{P_\lambda^0}{P_\lambda} \quad (10)$$

However, this may be affected by reflection and diffuse scattering. In ideal cases, where other factors are negligible, the absorbance of a material can also be expressed as a function of the optical length of the radiation within the material, as given by the Beer-Lambert law, Equation (11).<sup>[120]</sup>

$$A = \varepsilon lc \quad (11)$$

Where  $\varepsilon$  is the molar absorption coefficient of the material,  $l$  is the optical path length within the material, and  $c$  is the concentration of the material. When a material is irradiated, the valence band electrons can absorb photons with energies greater than the band gap ( $E_g$ ) of the material and be promoted to the conduction band. This band gap energy can thus be determined through the absorption spectra of the material using the Tauc analysis, Equation (12).<sup>[121]</sup>

$$(\varepsilon \cdot h\nu)^{\frac{1}{n}} = B(h\nu - E_g) \quad (12)$$

Where  $\varepsilon$  is the absorption coefficient,  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  J Hz<sup>-1</sup>),  $\nu$  is the frequency of the incident radiation,  $n$  is the parameter dependent on the nature of the transition,  $B$  is a constant (the slope of the linear Tauc plot), and  $E_g$  is the band gap energy.  $n$  can have the following values.<sup>[122-124]</sup>

1.  $n = 1/2$  for direct allowed transitions
2.  $n = 3/2$  for direct forbidden transitions
3.  $n = 2$  for indirect allowed transitions
4.  $n = 3$  for indirect forbidden transitions

Due to the proportionality of  $A$  and  $\varepsilon$  from Equation (11), the values can be substituted into the Equation. When this equation is plotted with the incident radiation energy ( $h\nu$ ) on the X-axis and the  $(\varepsilon \cdot h\nu)^{1/n}$  term on the Y-axis, the X-intercept of a tangent fitted across the linear region of the plot gives the  $E_g$ . However, for optically solid samples, such as powders and thin films, it is not possible to collect transmission or absorbance data. P. Kubelka and F. Munk instead proposed a function, Equation (13), which transforms the diffuse reflectance spectra to an absorption spectrum.

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1 - R_{\infty})^2}{2R_{\infty}} \quad (13)$$

Where  $R_{\infty}(= R_{sample}/R_{standard})$  is the reflectance of an infinitely thick sample measured from the diffuse reflectance spectroscopy (DRS),  $K$  is the absorption coefficient, and  $S$  is the scattering coefficient. The Kubelka–Munk function can then be used to replace  $\varepsilon$  in the Equation, yielding the Tauc plot for diffuse reflectance, as shown in Equation (14).<sup>[125]</sup>

$$(F(R_{\infty}) \cdot h\nu)^{\frac{1}{n}} = B(h\nu - E_g) \quad (14)$$

Due to the manual fitting of the linear region in a Tauc plot, there are possibilities for error in the value of  $E_g$  obtained from these measurements.

A Cary 5000 UV-Vis-NIR (Agilent) spectrophotometer equipped with an integrating sphere was used for the transmission and DRS measurements, and a Cary 60 UV-vis (Agilent) spectrophotometer equipped with a remote fibre optic diffuse reflectance accessory was used for automated measurements.

### 3.1.5 Photoelectron Spectroscopy in Air

The ionisation potential (i.e., energy of the valence band) of materials was measured using photoelectron spectroscopy in air (PESA). In this technique, monochromatic UV radiations are used to bombard the sample surface. When the energy of the incident radiation is sufficient to remove an electron from the sample, a photoelectron is emitted. These photoelectrons generate oxygen anions in the chamber, which are measured by a detector. In a plot of the incident photon energy against the yield of oxygen anions detected, the intercept between the slope and baseline counts gives the ionisation potential of the material. The slope of the plot depends on the shape of the density of states and the intensity of the incident photons. The data collected from photoelectron yield ( $Y$ ) against excitation energy ( $h\nu$ ) is fitted using a regression model (Equation (15)).

$$Y = (h\nu - IP)^n \quad (15)$$

For this thesis, an AC-2E (Riken Keiki Co. Ltd.) was used to collect the PESA data.

### 3.1.6 Atomic Force Microscopy

Atomic force microscopy (AFM) is a non-optical technique that physically maps the topography of a sample surface using a measuring tip, similar to profilometry. Due to the extremely small size of an AFM tip, the interactions between it and the sample surface enable the measurement of surface roughness with a spatial resolution of below 1 nm. An AFM tip consists of a cantilever with the actual measuring tip, which has a tapered end with a radius of curvature of a few nanometres. This is mounted on a silicon for ease of handling. As the AFM tip moves across the sample surface, the cantilever is deflected,

corresponding to the topography of the surface. These deflections are, in turn, measured by a laser focused on the back of the cantilever and reflected onto a photodetector. Both vertical and horizontal deflections of the cantilever can be measured from the photodetector signals. A force is exerted on the AFM tip as it nears the sample surface, based on which the AFM can be operated in various modes:

1. *Continuous contact*. The force experienced by the cantilever is maintained at a constant level using a feedback loop. In this scenario, the tip and sample surface experience high wear.
2. *Non-contact*. The tip is oscillated near its resonance frequency to precisely measure the force acting on it, ensuring it never comes into contact with the surface. Due to larger tip-to-sample distances, the measurement resolution is reduced.
3. *Tapping*. The tip vibrates continuously and only comes into contact with the surface briefly. A reduced level of wear is experienced in this scenario.

AFM for this thesis was done using a Dimension Icon (Bruker).

### 3.1.7 Raman Spectroscopy

C. V. Raman discovered the Raman effect, which is the inelastic scattering of light by a material. This effect is the basic principle behind Raman spectroscopy. When light is incident on a material, a tiny fraction of it normally undergoes elastic scattering (Rayleigh scattering) in random directions. However, an even smaller fraction of this incident light can be inelastically scattered (Raman scattering). These energy differences arise when an electron, which was excited by the incident light, relaxes to an energy state with a different vibrational energy. When the scattered photon loses energy, it is termed the Stokes shift, and the inverse, when it gains energy, is the anti-Stokes shift. This technique can be used to investigate molecular vibrations, structural transitions, the presence of defects like oxygen vacancies, and local chemical environments.

An inVia™ Raman confocal microscope (Renishaw) was used for the work in this thesis.

### 3.1.8 Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy

Infrared (IR) spectroscopy is used to obtain information about the molecular interactions in a material. Depending on the atoms present in a bond, the orientation of the bond vis-à-vis the rest of the molecule and the number of bonds, these bonds will have a characteristic vibration associated with them. IR spectroscopy differs from Raman spectroscopy in two ways: IR reports the wavenumber at which vibrational modes are present, compared to Raman, which detects the shift in vibration; IR absorption is possible only when there is a change in the dipole moment associated with the

vibrational mode, while Raman signals arise due to the polarizability of molecules. Over the whole range of the IR spectrum, different types of bond interactions can be studied.

1. *Far-IR* ( $400 - 10\text{ cm}^{-1}$ ). This provides information about the group vibrational modes of molecules and lattices.
2. *Mid-IR* ( $4000 - 400\text{ cm}^{-1}$ ). This is used to investigate the fundamental vibration modes of molecules.
3. *Near-IR* ( $14000 - 4000\text{ cm}^{-1}$ ). This can describe electronic transitions in molecules and overtones of vibrational modes.

A mathematical function, the Fourier transform, is utilised to translate the total energy of light detected into a spectrum of energy at different wavenumbers. The bands visible in this converted spectrum can be used to identify molecular vibrations based on their characteristic values.

To simplify the sample preparation and increase the speed of measurements, an accessory which uses attenuated total reflectance (ATR) was introduced to the traditional FTIR spectrometer. The use of total internal reflection mimicked the transmission spectra obtained from an FTIR spectrometer.<sup>[126]</sup> This extends the scope of IR spectroscopy to solid and liquid samples without the use of binding materials like KBr.

A Nicolet iS50 ATR-FTIR (Thermo Scientific) spectrometer was used for the work in this thesis.

### 3.1.9 Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy is a non-contact, non-destructive technique used for probing the interaction of light and matter through the photoexcitation of electrons in a material. When high-energy photons from a laser source are incident on a material, they cause the electrons in it to excite to higher energy states. The subsequent radiative relaxation of these excited electrons back to lower energy levels results in the emission of low-energy photons, known as photoluminescence. PL materialises as fluorescence, with more probable emissions having a faster decay rate between energy levels with the same spin, or phosphorescence, which involves emissions having a slow decay rate between energy levels with unpaired spin. PL can be recorded as an emission spectrum, where a fixed wavelength is used for excitation, and the PL intensity is measured as a function of wavelength. Alternatively, it can be recorded as an excitation spectrum, where the emission intensity is measured at a fixed wavelength as the excitation wavelength is varied. Details about the material's band structure, defect states and recombination mechanisms can be studied with the help of the PL spectra. PL measurements are carried out in one of two modes:

1. *Steady state*. In this, PL intensity is measured as a function of the wavelength of the emitted light under constant illumination. It is useful for materials where the PL intensity does not change quickly.
2. *Time-resolved*. In this process, the material is excited with short, high-energy pulses to measure the variation in PL intensity over time. This helps to understand the faster radiative relaxations taking place over very short time intervals.

### 3.1.10 Solar Cell Characterisation

A solar cell converts the energy of incident electromagnetic radiation into electrical energy. A solar simulator is used to replicate a standardised solar irradiation spectrum to study the behaviour of solar cells in a laboratory. The current density-voltage (JV) characteristics measured under illuminated and dark conditions are used to characterise solar cells. Figure 9 shows the JV characteristic curves for an ideal solar cell. The shift between the curves for illuminated and dark conditions is mainly due to the generation of photocurrent. The curve for the illuminated condition gives information about important parameters.<sup>[127]</sup>

1. *Short circuit current density ( $J_{SC}$ )*. The current density in the event of a short circuit,  $V = 0$  V (Y-intercept of the curve).
2. *Open circuit voltage ( $V_{OC}$ )*. The voltage reached with open terminals,  $J = 0$  mA cm<sup>-2</sup> (X-intercept of the curve).
3. *Maximum power point (MPP)*. The point at which maximum power is generated by the solar cell. The current density and voltage at this point are  $J_{MPP}$  and  $V_{MPP}$  respectively.
4. *Fill factor (FF)*. Equation (16) describes the ratio of the power at the MPP to the product of  $J_{SC}$  and  $V_{OC}$ . This is a visual representation of the losses due to recombination and transport.
5. *Power conversion efficiency (PCE)*. This is a critical parameter for understanding the quality of a solar cell. It is the ratio of electrical power at the MPP ( $P_{out}$ ) to the incident power irradiance ( $P_{in}$ ) as shown in Equation (17).

$$FF = \frac{J_{MPP}V_{MPP}}{J_{SC}V_{OC}} \quad (16)$$

$$PCE = \frac{P_{out}}{P_{in}} = \frac{J_{SC}V_{OC}FF}{P_{in}} \quad (17)$$

For the work in this thesis, a Lightline AX-LA 200 solar simulator (Sciencetech) was used.

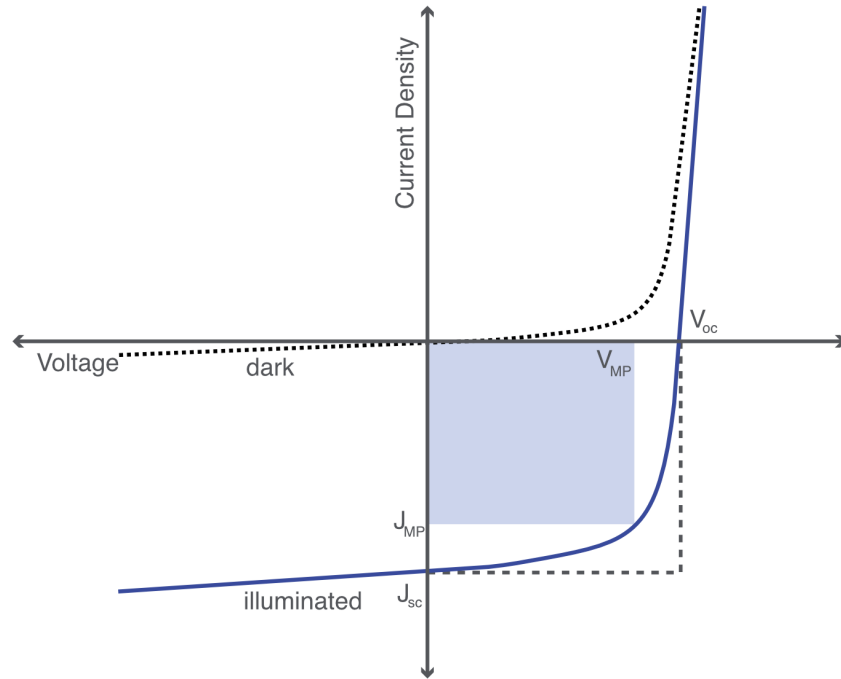


Figure 9: JV characteristics curve for a general PV device with the important parameters marked.

### 3.1.11 Hall Effect Measurement

The Hall effect, discovered by E. Hall in 1879, has become a standard technique for characterising the electronic charge carrier transport properties, such as carrier density, carrier mobility, and carrier type, in semiconducting materials.<sup>[128]</sup> The Hall effect is observed when a magnetic field and an electric current are applied perpendicularly to a sample, generating a transverse (i.e., out-of-plane) electric current and consequently a voltage, termed the Hall voltage, in response to both the magnetic field and the current. Since the calculation of the Hall voltage requires knowledge of resistivity and sample thickness, Hall measurements are typically combined with resistivity measurements using the van der Pauw technique, as both methods require similar sample geometries, as shown in Figure 10. Equation (18) describes the formula for calculating Hall mobility ( $\mu_H$ ).

$$\mu_H = \frac{|V_H t|}{BI\rho} \quad (18)$$

Here,  $V_H$  is the Hall voltage developed across the sample,  $t$  is the sample thickness,  $B$  is the magnetic field through the sample,  $I$  is the applied current, and  $\rho$  is the resistivity of the sample.

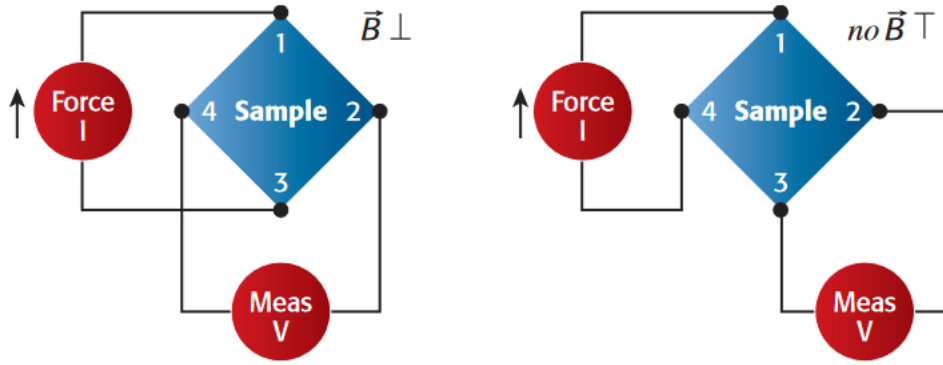


Figure 10: Configurations for (a) Hall voltage and (b) van der Pauw resistance measurement.<sup>[129]</sup>

Due to the 4-fold symmetric nature of the measurements, square-shaped samples are the most commonly used ones. Four probes are connected to each of the corners for measurements. As the measured parameters have a strong dependence on temperature and small values, multiple results are averaged to acquire accurate results. Figure 11 illustrates all the configurations used during each of the Hall voltage measurements, and Figure 12 does the same for van der Pauw resistance measurements.

Hall measurements were done using an HCS10 Hall Effect Measurement System (Linseis Messgeräte GmbH) for the work in this thesis.

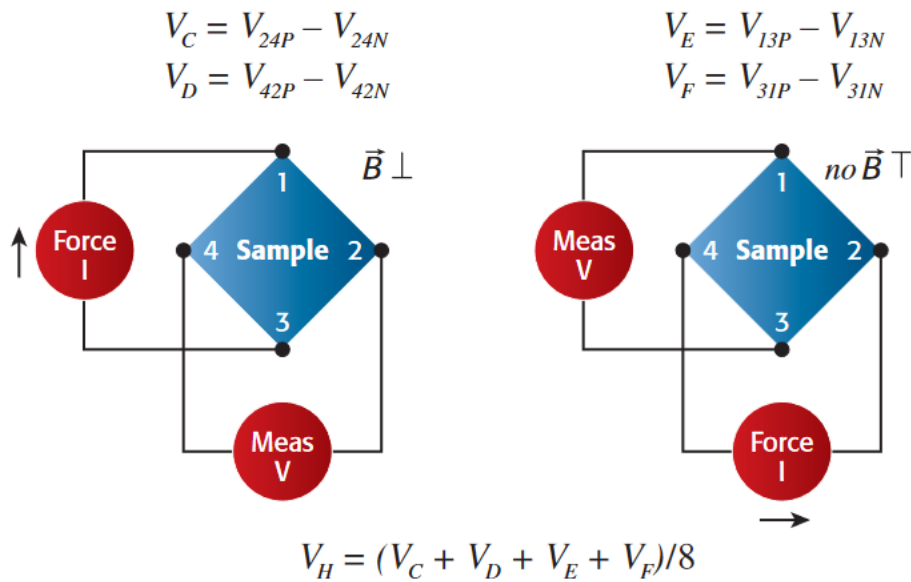


Figure 11: All the computations for the measurement of Hall voltage with different polarities of current and direction of magnetic field. The average of all these values is the measured Hall voltage.<sup>[129]</sup>



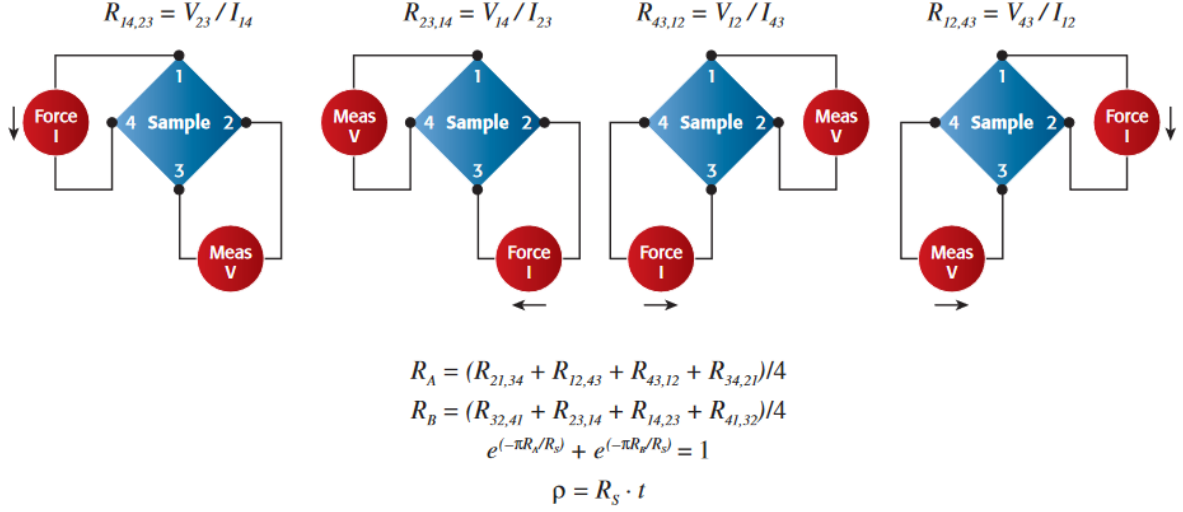


Figure 12: All the combinations used for the van der Pauw resistance measurements. These are averaged to obtain the resistivity of the material.<sup>[129]</sup>

### 3.1.12 Nanoindentation

Nanoindentation is a characterisation technique that utilises a very small, sharp tip to press into a material's surface, measuring its mechanical properties at the nanoscale. The tip is typically made from a hard material with known properties, such as diamond, and is subjected to a load, causing it to penetrate the sample surface. The hardness of the material can be calculated from Equation (19).

$$H = \frac{P_{max}}{A_r} \quad (19)$$

Here,  $H$  is the hardness of the material,  $P_{max}$  is the maximum applied load, and  $A_r$  is the residual indentation area. As small loads and tip sizes are frequently used for this, the residual area might be in the order of a few square micrometres or nanometres. As imaging this is cumbersome, a high-precision indenter with a known geometry is employed. In this work, a Berkovich tip with a three-sided pyramid geometry was used. Since the penetration depth is known, the indentation area can be calculated from the tip dimensions. Another important parameter that is calculated during nanoindentation is the Young's modulus,  $E$ . It quantifies the relationship between compressive/tensile stress applied to the material and the axial strain developed therein, within its linear elastic region. The stiffness of the material,  $S$ , is the slope of the load-displacement curve ( $dP/dh$ ) obtained during nanoindentation and can be used to calculate the Young's modulus.

An iNano Nanoindenter (KLA) was used for stiffness measurements in this work.

## 3.2 Synthesis Techniques

### 3.2.1 Mechanochemical Synthesis

Mechanochemical synthesis is quite attractive for the fabrication of HEMs, as it offers a straightforward one-step process that avoids the high temperatures usually required for their formation. This synthesis is done by using a high-energy planetary ball mill to mix the constituent precursors and induce phase formation. The impact between the milling media (tungsten carbide or zirconia balls) and the vial results in localised regions of high energy (shown in Figure 13), which is enough to facilitate the synthesis of HEMs. This technique has already been used to synthesise various high-entropy systems, such as oxides, oxyfluorides, and sulphides.<sup>[27,130,131]</sup> The atmosphere for the synthesis can also be controlled as the vials are sealed, allowing for the examination of air-sensitive compositions. The synthesis conditions can be further varied by controlling parameters such as the materials used for the vial and balls, the precursor-to-ball weight ratio, the rotational speed, and the milling duration. This synthesis typically yields homogeneously mixed nanoparticles with a high defect density as the product.

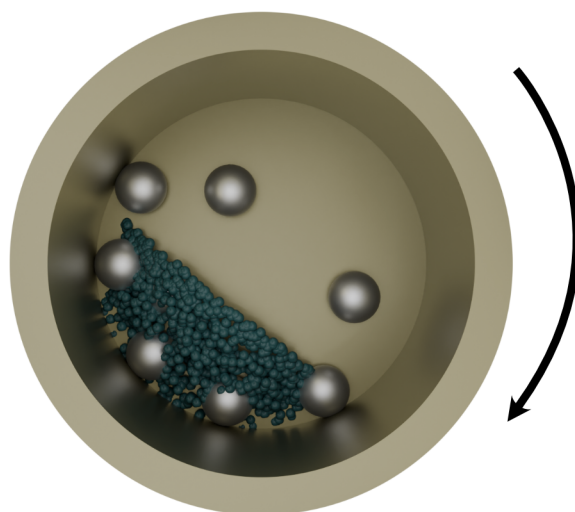


Figure 13: Schematic of a ball milling vial.

### 3.2.2 Modified Pechini Process

Sol-gel techniques have been a popular choice for synthesising nanoparticles of oxides, carbides, and nitrides. They enable control over composition, microstructure, and morphology, while still having high-purity products.<sup>[132]</sup> Figure 14 illustrates how different process parameters in the sol-gel process can help change properties of the final product. The modified Pechini process is a sol-gel technique that requires minimal equipment, and it has gained prominence for the synthesis of multicomponent systems. It is based on the synthesis of titanate dielectrics as described by Pechini in 1967.<sup>[133]</sup> It allows the use of a wide range of precursors and can be extended to thin-film deposition.

It starts off with making a homogeneously mixed aqueous solution of the cationic precursors, mainly nitrates, along with a polyalcohol and a chelating agent, like citric acid (the most commonly used agent) or EDTA (in case of basic cations like  $\text{Ba}^{2+}$ ). The metal cations form complexes with the chelating agent, which are then polymerised into a resin using the polyalcohol, most commonly ethylene glycol, through an esterification reaction. This method has been employed for multi-cationic systems as it is able to preserve the chemical homogeneity from the aqueous solution through the resin. A viscous polymeric resin is obtained after the evaporation of excess water by heating the precursor solution at temperatures in the range of 110 °C - 140 °C. This resin is further heated to 300 °C – 400 °C to remove unreacted organic precursors and initiate thermal decomposition. A metastable oxide phase is generally formed at this stage, especially in multi-cationic systems, which is then annealed at higher temperatures to obtain the final single-phase product. Figure 15 illustrates the various reactions involved in the modified Pechini process.

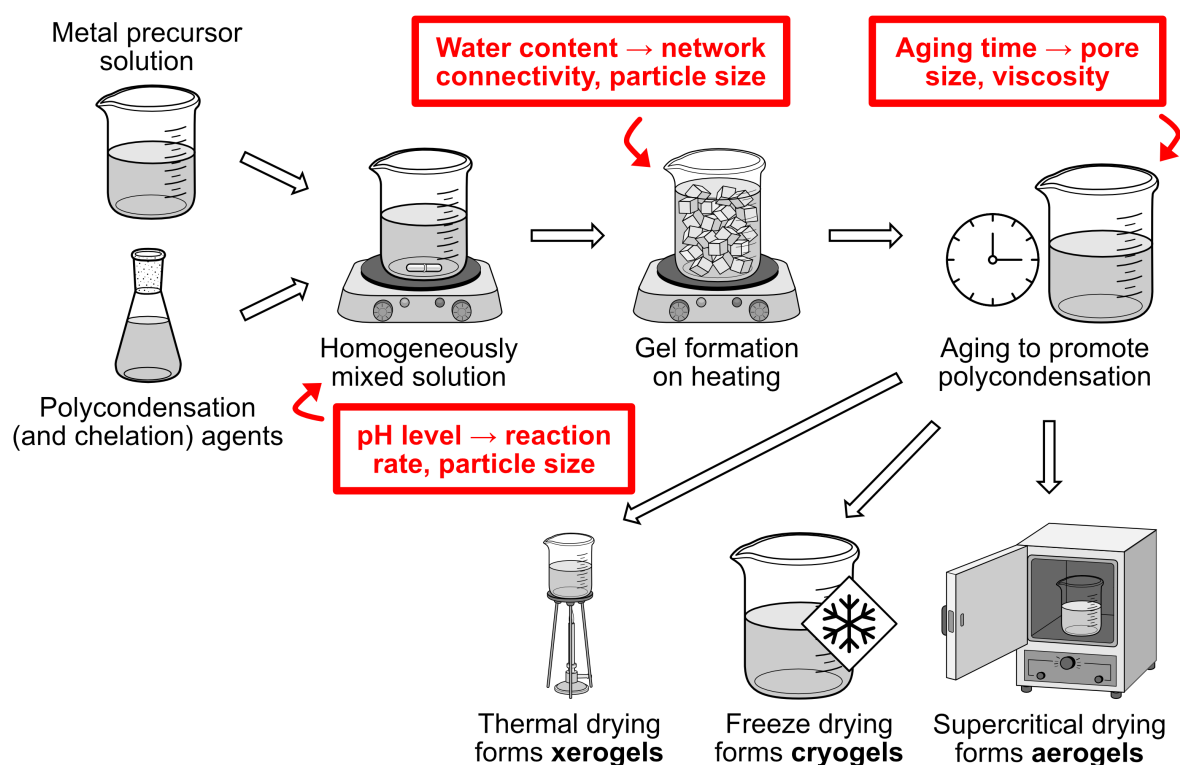


Figure 14: Schematic illustration of the sol-gel synthesis route, highlighting key factors affecting material properties. Reproduced with permission.<sup>[132]</sup> Copyright 2025, John Wiley and Sons.

The polymerised gel prepared in the modified Pechini process can also be used for thin film deposition via spin coating or dip coating.<sup>[134]</sup> The film obtained from the chelated solution is dried and pyrolysed to remove water and organic precursors. The viscosity of this solution can be increased by allowing it to age, ensuring maximum polymerisation has taken place. This is followed by heat treatment at higher temperatures to induce crystallisation of the final phase.

## Experimental Methods

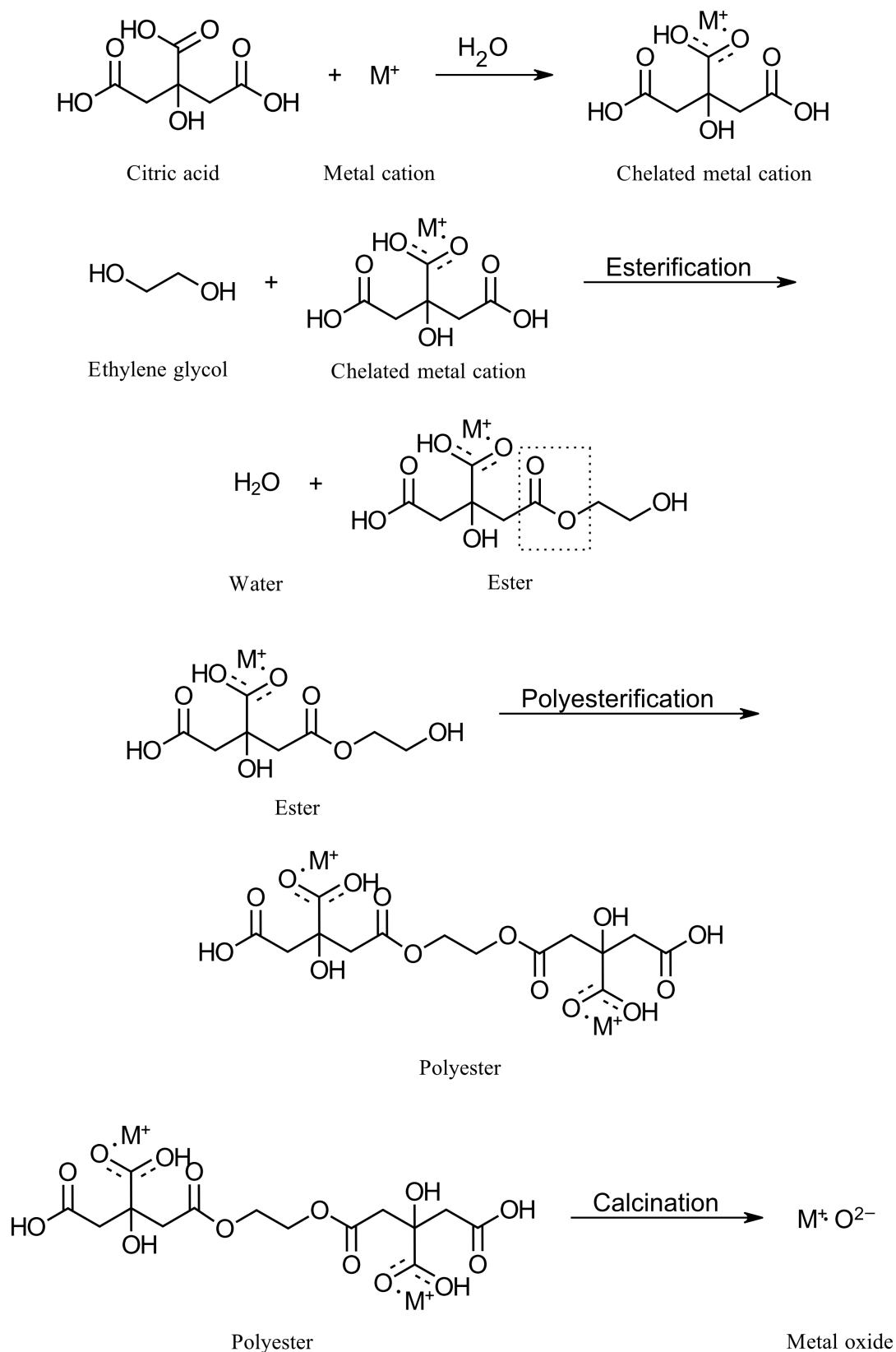


Figure 15: Reactions involved in the modified Pechini process.

### 3.2.3 Reverse Co-Precipitation

Reverse co-precipitation (RCP) is a simple wet-chemistry synthesis route often used to produce oxide nanoparticles and has also successfully produced a variety of HEOs. First, an aqueous solution is prepared by homogeneously mixing the cationic precursors, typically metal nitrates, in a large beaker. A strongly basic solution of NaOH or NH<sub>4</sub>OH is then slowly added dropwise to this precursor solution under constant stirring. This step is crucial to ensure that the final particles have a uniform size. The addition of a base to an acidic solution causes the precipitation of metal hydroxides, as shown in Equation (20). These precipitates are then separated from the solution by filtration, centrifugation, or drying. The dried precipitates are then calcined at high temperatures to promote phase formation, yielding the final oxide, as shown in Equation (21). Parameters such as the precipitant used, stirring speed during titration, titration rate, and pH can be used to influence the morphology and vacancy concentration of the final product, as schematically shown in Figure 16.

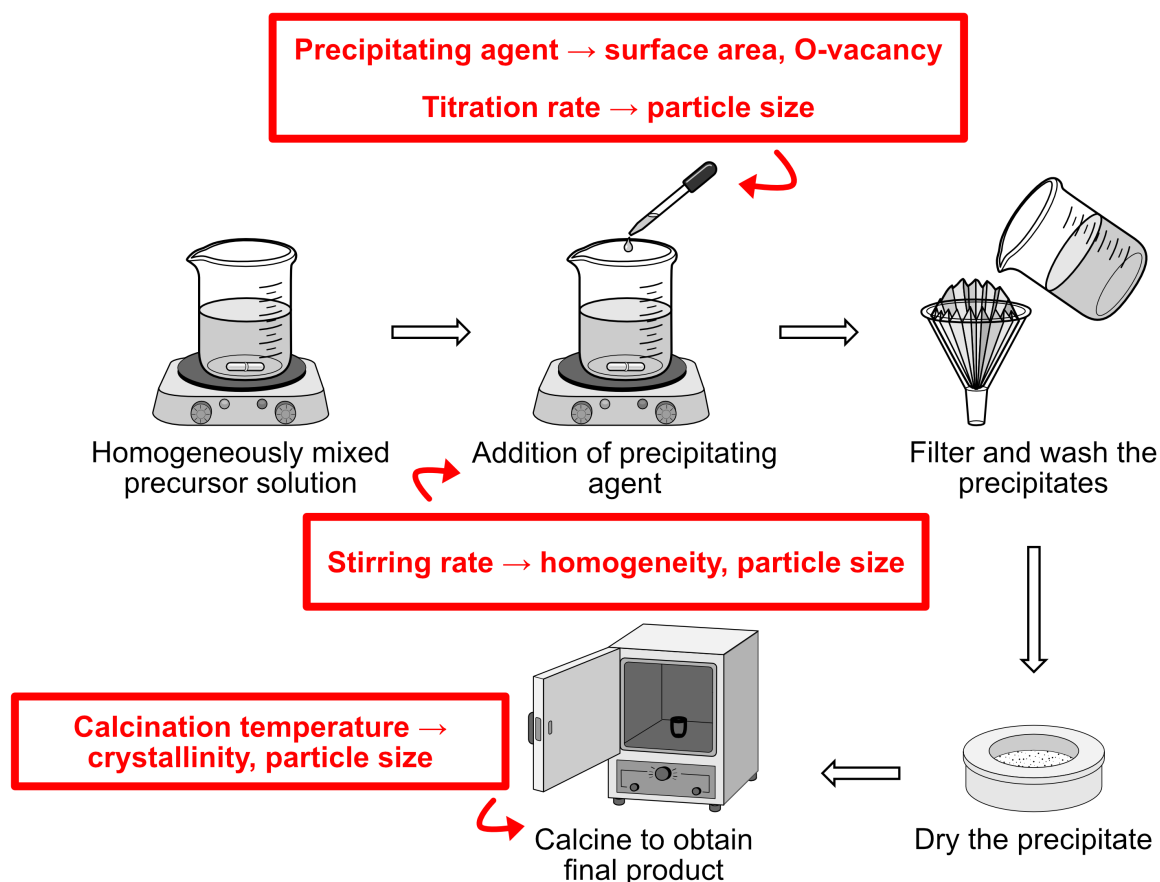
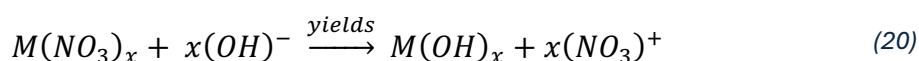


Figure 16: Schematic illustration of the co-precipitation synthesis route, highlighting key factors affecting material properties.<sup>[132]</sup> Copyright 2025, John Wiley and Sons.

### 3.2.4 Solid-State Synthesis

Solid-state synthesis is the simplest, albeit energy-intensive, technique for preparing HEOs at high reaction temperatures. It requires fewer process parameters and simpler equipment, enabling large-scale production and making it an attractive synthesis route. The direct reaction between solid-phase particles occurs at grain boundaries, where particles come into contact, as high temperatures enhance ionic diffusion kinetics. The precursors are often milled before annealing to ensure homogeneity and smaller particles for enhanced reactivity. The precise regulation of diffusion-controlled reactions remains challenging, thereby constraining product purity. In complex systems, there is a higher possibility of the formation of side-phases or incomplete reactions, as the reaction rates for all components differ.

### 3.2.5 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a commonly used physical vapour deposition technique for growing oxide thin films. It has been used to prepare oxide thin films with various crystal structures, ranging from simple rock-salt structures to more complex layered or Ruddlesden–Popper cuprate structures. Figure 17 illustrates the operation of the PLD system. A high-energy pulsed laser is used to ablate a densely packed target material with the exact stoichiometry as the desired product. This results in the evaporation of the target, forming a plasma plume that is then deposited onto a heated substrate as a thin film. The partial pressure of oxygen in the vacuum chamber is crucial for controlling oxygen vacancies in the thin films and ensuring the correct stoichiometry in the product. Other parameters, such as laser fluence, deposition temperature, and the substrate used, also play a crucial role in determining the properties of the thin film. The target for preparing HEO thin films is obtained by pressing the desired oxide into a pellet using a uniaxial hydraulic press. These are then sintered at high temperatures to get a highly dense pellet, which is crucial for ensuring homogeneity in the plasma plume and, consequently, the thin film.



Figure 17: Illustration of the PLD mechanism.



## 4 Synthesis and Characterisation of Novel High-Entropy Low-Dimensional Perovskite-Derivative Halides

The rapid rise of metal halide perovskite solar cells has been driven mainly by the exceptional optoelectronic properties of lead-based perovskites, including tunable band gaps, long carrier diffusion lengths, and defect tolerance.<sup>[135]</sup> However, the practical deployment of these materials remains hindered by two persistent challenges: the toxicity associated with lead and the intrinsic instability of organic lead-halide frameworks under environmental stressors such as moisture, heat, and illumination. These limitations have motivated intensive research into alternative absorber materials that can replicate the favourable band structure and electronic behaviour of Pb-perovskites while offering superior stability and reduced environmental impact.<sup>[136,137]</sup> Among the wide range of lead-free candidates,  $A_3Bi_2I_9$ -type materials have emerged as an attractive starting point due to their structural relationship to the perovskite family and their ability to host diverse chemical substitutions.<sup>[138]</sup>

This work investigates the application of a HE design approach to the  $MA_3Bi_2I_9$  lattice, aiming to engineer novel multicomponent systems that more closely emulate the optoelectronic characteristics of lead-based perovskites. Organic cations, such as methylammonium ( $CH_3NH_3^+$ ), play a crucial role in stabilising the crystal lattice, modifying the band structure, and influencing charge-carrier transport in these systems.<sup>[139,140]</sup> The incorporation of multiple cations at the B-site is expected to increase configurational disorder and broaden the accessible electronic landscape, enabling controlled tuning of band structure, defect energetics, and carrier transport. This strategy is motivated by the hypothesis that introducing compositional complexity can compensate for the inherent limitations of conventional Bi-based perovskites, particularly their wider band gaps and less favourable carrier dynamics, while simultaneously enhancing structural resilience.

Additional complexities are expected to arise when expanding the HEM concept to iodides, particularly in integrating organic components. The low decomposition temperatures of organic molecules constrain the energy input during synthesis to prevent degradation during high-energy processes, and their increased sensitivity to environmental conditions and solvents limit solution-based synthesis techniques. Unlike purely inorganic high-entropy compounds, hybrid organic-inorganic systems require consideration of hydrogen bonding and steric effects, which can favour specific orientational arrangements, as well as electronic interactions between organic and inorganic sublattices. This additional degree of compositional freedom broadens the



range of tunable properties and presents new challenges in understanding the structure-property relationships in these materials.<sup>[64,65]</sup>

This chapter discussed the synthesis, structural analysis, and optoelectronic evaluation of a series of high-entropy low-dimensional perovskite-derived materials designed as potential lead-free absorber candidates. By comparing their properties to both the parent compound and to archetypal lead-based perovskites, it is aimed to assess the extent to which high-entropy design can bridge the performance gap and advance the development of stable, environmentally conscious alternatives for next-generation photovoltaics.

## 4.1 Materials Synthesis

### 4.1.1 Powder Preparation

Perovskite derivative high-entropy iodides based on  $\text{MA}_3\text{Bi}_2\text{I}_9$  were synthesised using a mixture of cations substituting Bi at the B-site lattice positions. Sn, Ag, Bi, Cu, Sb, Ca, Na, and In were chosen as the compositional space for selecting the B-site cations, as they have ionic radii similar to those of  $\text{Bi}^{3+}$  (Table 1 lists the effective ionic radii of the cations chosen with a coordination number of 6). Specifically,  $\text{Sn}^{2+}$ ,  $\text{In}^{3+}$ , and  $\text{Sb}^{3+}$  were selected as their electronic configurations and ionic sizes are comparable to  $\text{Bi}^{3+}$ .  $\text{Ag}^+$ ,  $\text{Cu}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$  were included to compensate for charge imbalances and ensure overall charge neutrality, while maintaining similar ionic radii. These elements were also chosen as the structural stability of their paired systems has already been extensively studied. For instance, element pairs such as Ag-Bi, Cu-In, and Ag-Sb have been successfully incorporated into perovskite structures, demonstrating stability, small band gaps ( $<1.5$  eV), and electron mobilities similar to those of  $\text{MAPbI}_3$ .<sup>[141]</sup> Drawing upon these established findings, the behaviour of these element combinations can be extrapolated to predict their behaviour within the high-entropy framework, as fundamental structure-function relationships are generally retained across high-entropy systems. This careful balance of oxidation states and the preservation of similar ionic radii maximise the chances of synthesising stable single-phase high-entropy materials.

Eight different compositions (mentioned in Table 2) of high-entropy iodides (HEIs) were synthesised using these cations, with four compositions having five cations at the B-site and four compositions having six cations at the B-site. As  $\text{Sn}^{2+}$  is the cation most like  $\text{Pb}^{2+}$  in its electronic configuration and the Ag-Bi pair has shown the most potential in double-perovskite systems, these three cations have been included in each of the high-entropy compositions. The other cations are chosen to ensure charge balance in the system.

Table 1: Effective ionic radii of the selected precursor cations.

| Precursor Cation | Ionic Radii (Å) |
|------------------|-----------------|
| $\text{Bi}^{3+}$ | 1.03            |
| $\text{Sn}^{2+}$ | 1.02            |
| $\text{Sb}^{3+}$ | 0.76            |
| $\text{In}^{3+}$ | 0.8             |
| $\text{Ag}^+$    | 1.15            |
| $\text{Cu}^+$    | 0.77            |
| $\text{Na}^+$    | 1.02            |
| $\text{Ca}^{2+}$ | 1               |

Table 2: Synthesised triple perovskite derivative HEIs.

| Acronym | Composition                                                                                                                                |
|---------|--------------------------------------------------------------------------------------------------------------------------------------------|
| HEI-1   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.2}\text{Ag}_{0.2}\text{Bi}_{0.2}\text{Cu}_{0.2}\text{Sb}_{0.2})_2\text{I}_9$                      |
| HEI-2   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.16}\text{Ag}_{0.16}\text{Bi}_{0.16}\text{Cu}_{0.16}\text{Sb}_{0.16}\text{Ca}_{0.16})_2\text{I}_9$ |
| HEI-3   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.2}\text{Ag}_{0.2}\text{Bi}_{0.2}\text{Na}_{0.2}\text{Sb}_{0.2})_2\text{I}_9$                      |
| HEI-4   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.16}\text{Ag}_{0.16}\text{Bi}_{0.16}\text{Na}_{0.16}\text{Sb}_{0.16}\text{Ca}_{0.16})_2\text{I}_9$ |
| HEI-5   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.2}\text{Ag}_{0.2}\text{Bi}_{0.2}\text{Cu}_{0.2}\text{In}_{0.2})_2\text{I}_9$                      |
| HEI-6   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.16}\text{Ag}_{0.16}\text{Bi}_{0.16}\text{Cu}_{0.16}\text{In}_{0.16}\text{Ca}_{0.16})_2\text{I}_9$ |
| HEI-7   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.2}\text{Ag}_{0.2}\text{Bi}_{0.2}\text{Na}_{0.2}\text{In}_{0.2})_2\text{I}_9$                      |
| HEI-8   | $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.16}\text{Ag}_{0.16}\text{Bi}_{0.16}\text{Na}_{0.16}\text{In}_{0.16}\text{Ca}_{0.16})_2\text{I}_9$ |

Mechanochemical synthesis, specifically high-energy ball milling, was used to prepare the HEIs, as it has been successfully used to synthesise high-entropy fluorides previously.<sup>[130]</sup> The following chemicals were purchased from commercial sources and used as precursors without any further purification:  $(\text{CH}_3\text{NH}_3)\text{I}$  (Ossila, >99.9%),  $\text{AgI}$  (Sigma-Aldrich, 99%),  $\text{BiI}_3$  (Sigma-Aldrich, 99%),  $\text{CuI}$  (Sigma-Aldrich, 98%),  $\text{SbI}_3$  (Sigma-Aldrich, 98%),  $\text{CaI}_2$  (Sigma-Aldrich, 99%),  $\text{InI}_3$  (Sigma-Aldrich, 99.998%),  $\text{NaI}$  (Alfa Aesar,

>99.5%), and  $\text{SnI}_2$  (Thermo Scientific, >99%). Equimolar stoichiometric amounts of the precursors were mixed and milled in a tungsten carbide (WC) ball-milling vial with WC balls as the milling media, using a 20:1 ball-to-powder weight ratio. The vials were prepared and sealed in an argon-atmosphere glovebox (Jacomex, 10 ppm  $\text{O}_2$  and <1 ppm  $\text{H}_2\text{O}$ ) to maintain an argon atmosphere within the vials, thereby preventing material degradation from environmental factors. The precursors were ball-milled at 500 RPM in a ball mill (Retsch PM100) for a total of 48 hrs. Recurrent 10-minute pauses were used after 10 minutes of milling to prevent sample overheating, along with directional changes to ensure more homogeneous mixing. The ball milling product was used as the final powder sample. To observe the structural evolution of the precursors during ball milling, a separate batch of HEI-1 was milled at speeds increasing from 100 RPM to 500 RPM.

#### 4.1.2 Thin-film Preparation

The as-prepared ball-milled powders were dissolved in a 1:1 (v/v) mixture of dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) to obtain a 1 M precursor solution for spin coating. Other 1M solutions using only DMF, only dimethyl sulfoxide (DMSO), and mixtures of DMF, DMSO, and NMP were also prepared for testing. The indium-tin oxide (ITO) glass substrates used for spin coating were cleaned with water, acetone, and isopropanol for 15 minutes, followed by a 5-minute plasma treatment. 40  $\mu\text{L}$  of the prepared solution was spin-coated onto the substrate in a glovebox under an argon atmosphere. This substrate was then dried on a hot plate at 110  $^\circ\text{C}$  inside the glovebox to obtain an HEI thin film.

Usually, metal-organic halides are prepared by dissolving the iodide precursors in a solvent and spin-coating the mixture to form a thin film with the desired composition. To evaluate whether this approach is also applicable to high-entropy iodides, a 1 M solution containing the corresponding precursor iodides (without any ball milling) in a 1:1 (v/v) mixture of DMF and NMP was prepared for HEI-1. 40  $\mu\text{L}$  of this solution was spin-cast onto plasma-treated ITO glass substrates at 3000 RPM for 30 s in a glovebox under argon, and the substrates were then dried at 110 $^\circ\text{C}$  on a hot plate.

#### 4.1.3 Pellet Preparation

The powders obtained by ball milling were pressed into 8 mm pellets at 200 MPa using a uniaxial press for morphological investigations.

#### 4.1.4 Solar Cell Fabrication

Solar cells with HEI-1 as the absorber layer were fabricated, along with reference solar cells made from  $\text{MAPbI}_3$ . The HTL was deposited by spin-coating (2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl)phosphonic acid (MeO-2PACz; 60  $\mu\text{L}$ , 4000 RPM, 15 s) onto cleaned ITO glass substrates that had been plasma-treated for 15 min. The films were then annealed (100  $^\circ\text{C}$ , 18 min) to remove any water residues. HEI-1 powder was dissolved in

a 1:1 (v/v) mixture of DMF and NMP to form a 1 M solution. This solution was spin-coated (60  $\mu$ l, 5000 RPM, 35 s) atop the MeO-2PACz film. 10 s after the full rotational speed was attained, the film was washed with an antisolvent, diethyl ether (DEE, 400  $\mu$ l). They were then annealed on a hot plate (100  $^{\circ}$ C, 30 min) until the films turned dark red in colour. After sample annealing, a solution of [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM, 40  $\mu$ l, 20 g/l in chlorobenzene) was spin-coated (1000 RPM, 30 s followed by 4000 RPM, 10 s) on top of the HEI film. Bathocuproine (BCP, 60  $\mu$ l, 0.5 g/l in ethanol) was spin-coated (4000 RPM, 10 s) on top of PC<sub>71</sub>BM to complete the ETL. Finally, Ag was thermally evaporated through a shadow mask to form the top electrode ( $10^{-6}$  mbar, layer thickness 100 nm).

A 1.5M MAPbI<sub>3</sub> reference solution was prepared by dissolving MAI and PBI<sub>2</sub> in an equimolar ratio in a 875:125 (v/v) solution of DMF and DMSO. The MAPbI<sub>3</sub> solution was spin-coated (60  $\mu$ l, 5000 RPM, 35 s) atop the MeO-2PACz film and then annealed (100  $^{\circ}$ C, 60 min). The ETL and Ag deposition steps were identical to those of the HEI-1 solar cells.

## 4.2 Structural and Compositional Analysis

### 4.2.1 Crystallographic Analysis

#### 4.2.1.1 Powder Analysis

The MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> crystal structure consists of inorganic bismuth-iodide units and organic (CH<sub>3</sub>NH<sub>3</sub>)<sup>+</sup> cations. The structure features Bi<sub>2</sub>I<sub>9</sub> dioctahedra, where each Bi<sup>3+</sup> ion is coordinated by six iodide ions, forming face-sharing [BiI<sub>6</sub>] octahedra (as shown in Figure 18(a)). These Bi<sub>2</sub>I<sub>9</sub> units can create either a layered (2D) or zero-dimensional (0D) structure, depending on the polymorph. The (CH<sub>3</sub>NH<sub>3</sub>)<sup>+</sup> cations are situated between the bismuth-iodide units, where they help stabilise the structure through electrostatic interactions and hydrogen bonding with the iodide ions. In 3D perovskite structures (e.g., MAPbI<sub>3</sub>), the organic cation primarily adjusts the geometry of the 3D corner-sharing BX<sub>6</sub> network, leading to octahedral tilting and helping determine the stable polymorph based on symmetry. In MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub>, (CH<sub>3</sub>NH<sub>3</sub>)<sup>+</sup> plays a role in organising the packing, affects the dimensionality (0D or 2D), and can significantly impact both optical and electronic properties. The rotational freedom and orientational disorder associated with the (CH<sub>3</sub>NH<sub>3</sub>)<sup>+</sup> cations can also affect the band edges and, in some cases, broaden the absorption spectra.

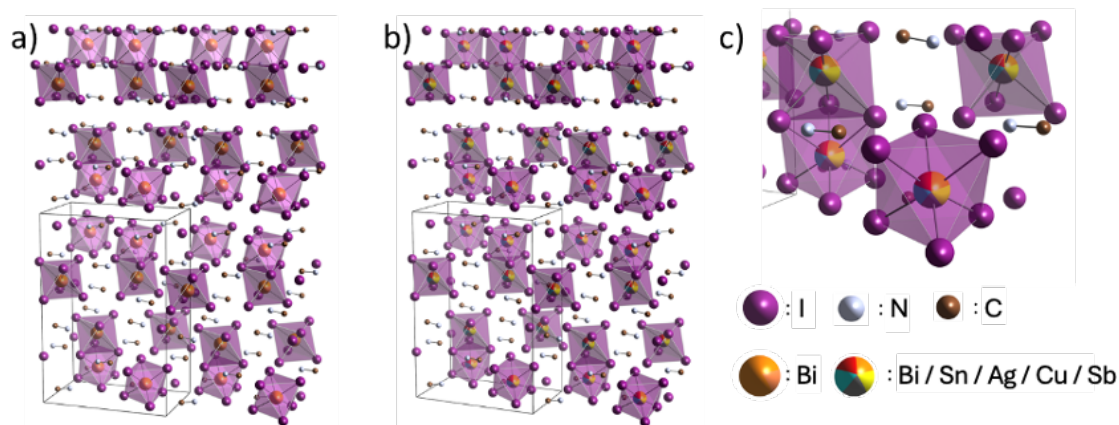


Figure 18: (a) Crystal structure of  $MA_3Bi_2I_9$ .  $Bi^{3+}$  ions are coordinated to  $I^-$  ions, forming a molecular complex that is distinctively isolated rather than forming extended networks or layers. The  $[Bi_2I_9]^{3-}$  units are characterised by a unique arrangement where two  $Bi^{3+}$  ions are connected by bridging  $I^-$  ions, creating a symmetrical structure. The discrete molecular units spatially separated by the organic cations form a 0D structure that allows for minimal interaction between the  $[Bi_2I_9]^{3-}$  units. (b) High-entropy triple perovskite derivative. Other elements partially replace the  $Bi^{3+}$  positions, while the crystal structure remains intact. (c) Detailed representation of the high-entropy  $[Bi_2I_9]^{3-}$  units. Figures created using Vesta.<sup>[142]</sup>

Table 3: The tolerance factor ( $t$ ), octahedral factor ( $\mu$ ), and the oxidation state weighted tolerance factor ( $\tau$ ) for the proposed compositions.

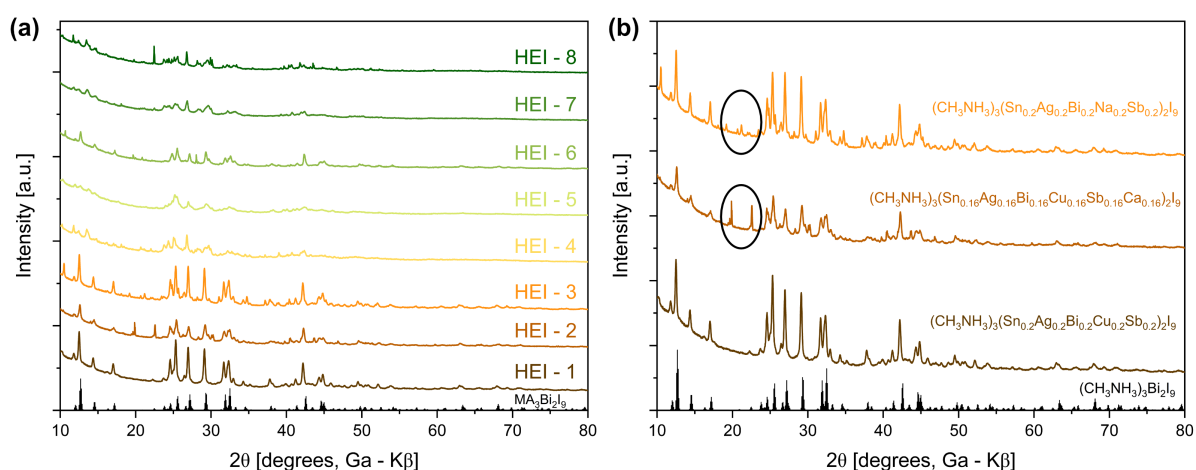
| Sample name | Tolerance factor ( $t$ ) | Octahedral factor ( $\mu$ ) | Oxidation tolerance factor ( $\tau$ ) |
|-------------|--------------------------|-----------------------------|---------------------------------------|
| HEI-1       | 0.70                     | 0.43                        | 4.09                                  |
| HEI-2       | 0.70                     | 0.43                        | 4.07                                  |
| HEI-3       | 0.70                     | 0.45                        | 4.01                                  |
| HEI-4       | 0.70                     | 0.45                        | 4.01                                  |
| HEI-5       | 0.70                     | 0.43                        | 4.08                                  |
| HEI-6       | 0.70                     | 0.44                        | 4.06                                  |
| HEI-7       | 0.70                     | 0.46                        | 4.00                                  |
| HEI-8       | 0.70                     | 0.46                        | 4.00                                  |

Geometric descriptors such as the tolerance factor and octahedral factor, commonly used to predict the structural stability of conventional 3D perovskites (as mentioned in Section 2.2.1), are not directly applicable to derivative compounds like  $MA_3Bi_2I_9$ , which lack a continuous 3D network. However, new tolerance factors have been proposed that may offer insights into the stability of low-dimensional perovskite-derived structures.<sup>[90]</sup> Table 3 presents the tolerance factor, octahedral factor, and oxidation tolerance factor

for the selected HEI compositions. These values were calculated using the Shannon radii for the cations and anions, with the ionic radius for  $(\text{CH}_3\text{NH}_3)^+$  taken as 2.16 Å based on standard literature values. As anticipated, both the tolerance and octahedral factors fall on the lower end of the stability range for conventional perovskite structures. Additionally, the oxidation tolerance factor is below 4.18, suggesting that a perovskite-like structure or derivatives are still feasible.

The crystal structures of the synthesised HEIs were characterised using powder XRD measurements, collected using a Stadi P diffractometer (STOE), equipped with a Ga-jet X-ray source (Ga- $\text{K}\beta$  radiation,  $\lambda = 1.2079$  Å). The patterns were measured in the reflection mode, between 10 and 80° with a 0.02° step size. The powders were fixed with Kapton foil to protect against atmospheric degradation.

For the prepared HEIs, the measured XRD diffractograms correspond to the  $\text{MA}_3\text{Bi}_2\text{I}_9$  structure (ICSD database code 242181), as expected, which is a 0D structure with the space group  $C12/c1$ . Figure 18(b) and Figure 18(c) illustrate how the mixed cations occupy the B-site lattice points. HEI-1, HEI-2, and HEI-3 predominantly exhibit a single-phase structure similar to  $\text{MA}_3\text{Bi}_2\text{I}_9$ ; the remaining compositions are either multiphase or not clearly defined crystallographically in commercially available databases. These impurity phases may arise from the formation of metastable intermediate metal iodides. Figure 19(a) provides an overview of all compositions, while Figure 19(b) presents a more detailed view of the predominantly single-phase materials. HEI-2 and HEI-3 show additional reflections (indicated by ellipses), whereas HEI-1 exhibits the highest phase purity and crystallinity owing to its sharper peaks.



**Figure 19:** (a) XRD patterns of the synthesised compounds. While HEI-1, HEI-2, and HEI-3 exhibit a predominant  $C12/c1$  structure, the other compositions display significantly reduced crystallinity, which challenges the determination of their structure. (b) More detailed XRD patterns of HEI-1, HEI-2, and HEI-3. HEI-1 shows the highest purity and crystallinity. All compositions show the  $C12/c1$  structure; some additional reflections are found close to  $2\theta=20^\circ$  as marked.

Space group:  $C2/c$ ;  $a = 8.562(3) \text{ \AA}$ ,  $b = 14.802(5) \text{ \AA}$ ,  $c = 21.6522(6) \text{ \AA}$ ,  $V = 2744.26(1.44) \text{ \AA}^3$

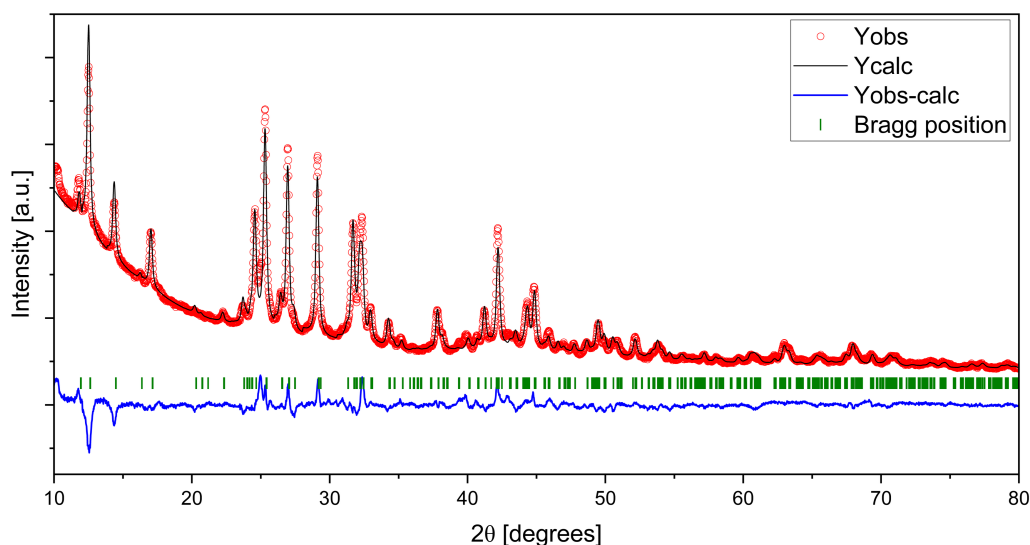


Figure 20: Rietveld refinement of the powder X-ray diffraction pattern of HEI-1.

Rietveld refinement was carried out with the  $C12/c1$  structure as a reference, as shown in Figure 20, confirming the formation of a single-phase structure. The structure exhibits a distorted lattice with a cell volume 1.25% larger than the ideal  $(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9$  structure. The  $R_{\text{wp}}$  was 4.86, and the goodness-of-fit was 4.47 for the refinement.

#### 4.2.1.2 Stability Against Environmental Degradation

Metal-organic halides are known to be highly chemically unstable, readily decomposing upon exposure to air or moisture. To assess the environmental stability of the synthesised HEIs, a powder sample of HEI-1 was stored under ambient laboratory conditions for 8 weeks, while a second sample was maintained in a high-humidity environment to evaluate moisture tolerance. The corresponding XRD diffractograms from a Cu-K $\alpha_{1,2}$  source diffractometer (Bruker, D8 Advance) are presented in Figure 21. The air-exposed sample was measured as is, while the sample stored within the glovebox was measured with an airtight specimen holder with a polymethyl methacrylate (PMMA) dome. The sample preserved under ambient conditions retained its crystallographic features over the whole 8-week period, indicating satisfactory stability. Some new low-intensity reflections, marked with an asterisk (\*), appeared, indicating the formation of a small amount of a secondary phase. In contrast, the sample exposed to elevated humidity degraded rapidly within 24 h, indicating poor moisture resistance. The zero-dimensional arrangement of the crystal structure has previously been shown to mitigate oxygen-induced degradation, as the isolated dimers are less prone to ion migration, which plagues 3D networks, a trend consistent with the present observations.<sup>[143]</sup> Overall, the HEIs exhibit greater stability than MAPbI<sub>3</sub>, though encapsulation remains necessary for practical device applications.



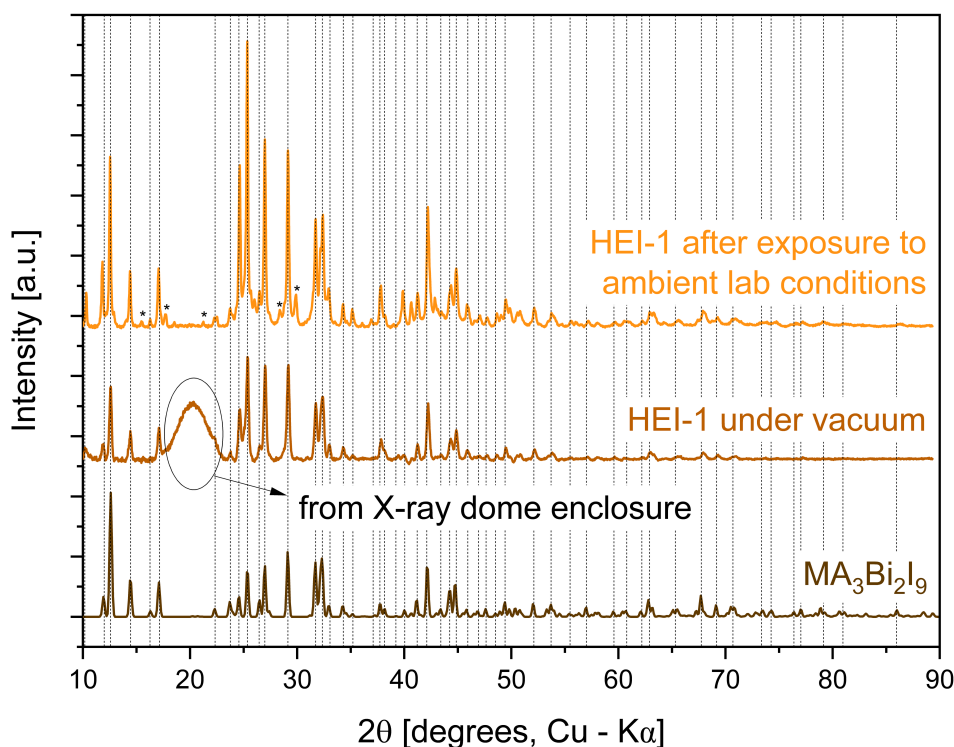


Figure 21: Comparison of XRD patterns for HEI-1 samples preserved under inert conditions (inside an argon-atmosphere glovebox) and under ambient lab conditions for a duration of 8 weeks. The asterisks mark new reflections appearing after exposure to air.

#### 4.2.1.3 Structural Evolution During Ball Milling

Mechanochemical approaches have previously been employed for the synthesis of  $\text{MAPbI}_3$ .<sup>[144]</sup> Owing to the softness of the initial materials and the low activation energy associated with the  $\text{MAI} - \text{PbI}_2$  reaction, ball milling at relatively low rotational speeds for only a few hours is generally sufficient to produce the final perovskite phase. In contrast, applying analogous milling conditions to the synthesis of HEIs yielded only a heterogeneous mixture of precursor iodides, indicating a substantially higher activation energy barrier for phase formation.

Figure 22 illustrates the evolution of crystallographic features as the milling speed is progressively increased, allowing for a more precise assessment of phase development with enhanced milling power and the associated energy transfer resulting from thermally activated collision events. To monitor the structural evolution during mechanochemical synthesis, small aliquots (on the order of a few micrograms) were periodically extracted from the milling jar at predefined time intervals and analysed by XRD. The aliquot mass was kept minimal to avoid perturbing the ball-to-powder ratio.



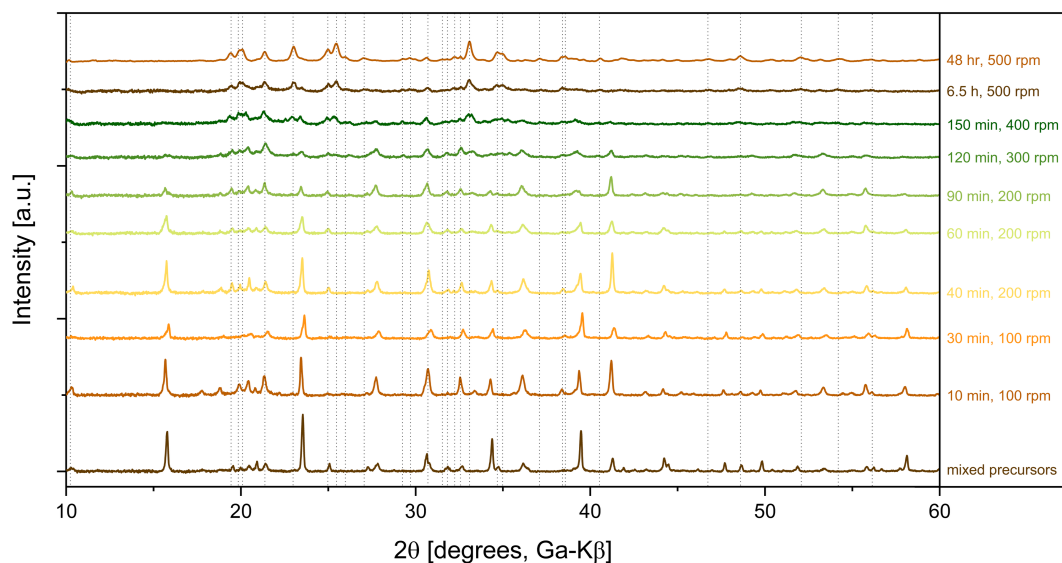


Figure 22: Structural development of HEI-1 during the mechanochemical synthesis; the dotted lines mark the major peaks associated with the structure of  $\text{MA}_3\text{Bi}_2\text{I}_9$ . The signatures of the mixed precursors are visible in the XRD pattern up to a rotation speed of 300 RPM. At higher rotation speeds, the C12/c1 structure forms.

The XRD results demonstrate that both extended milling durations and high rotational speeds are required to obtain the high-entropy iodides in the desired phase. At lower milling speeds ( $\leq 300$  RPM), the diffraction patterns exhibit reduced intensities and modest peak broadening, which is attributed to the reduction in crystallite size of the precursor materials; however, no evidence of transformation to the target phase is observed. Initial signs of structural conversion emerge at 300–400 RPM, with similar diffraction features persisting at 500 RPM. Ultimately, prolonged milling for 48 h at 500 RPM was necessary to produce broad but discernible reflections characteristic of the  $\text{MA}_3\text{Bi}_2\text{I}_9$ -type structure.

Mechanochemical synthesis facilitates the stabilisation of low-dimensional perovskite derivative high-entropy iodides; however, achieving phase-pure products requires both high milling energy and prolonged processing times, underscoring the delicate interplay between entropy-driven cation mixing and the inherent constraints of crystallographic stability.

#### 4.2.1.4 Thin-Film Analysis

Thin films of the synthesised HEI compositions prepared by spin-coating were characterised using grazing incidence XRD using an Empyrean 3 (Malvern Panalytical) with a  $\text{Cu-K}\alpha_{1,2}$  source and PIXcel<sup>1D</sup> detector with an incident angle of  $1^\circ$ .

The diffraction pattern for the thin film prepared by spin-coating the mixed iodide precursor solution for HEI-1 is shown in Figure 23(a). The reflections do not correspond with the expected  $\text{MA}_3\text{Bi}_2\text{I}_9$  structure. The reflections instead belong to either the chosen

precursor iodides or some intermediary phases. This implies that the HEI phase requires a larger amount of energy compared to a simpler organometallic halide to crystallise.

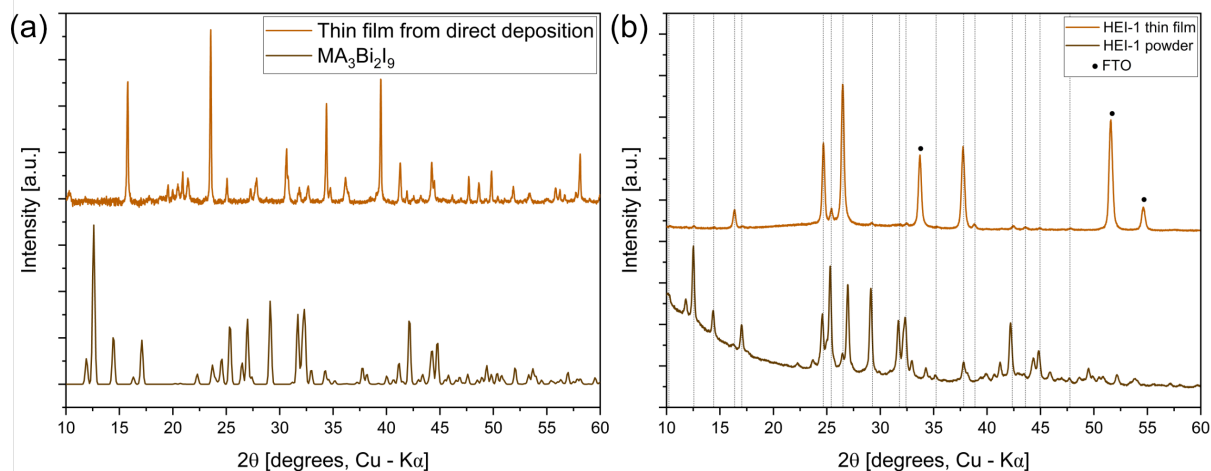


Figure 23: (a) XRD patterns of the thin film prepared by spin-coating a solution of mixed iodide precursors for HEI-1, and (b) Comparison of the XRD patterns for the HEI-1 thin film prepared by spin-coating and the powder used to make the solution.

The thin films later prepared by dissolving the synthesised HEI powders exhibit a significantly improved crystallisation behaviour, as seen for HEI-1 in Figure 23(b). The peaks observed in its diffraction pattern coincide with those from the powder obtained by high-energy ball milling, indicating that the structure is retained. The reflections have mismatched intensities, which may arise from the growth of an oriented thin film. Given that the iodide precursors and the synthesised HEI powders dissolve completely in the solvent based on the transparency of the solution, it can be inferred that the high-energy ball-milling might have caused changes in the oxidation state of some cationic species that are conserved upon dissolution, helping lower the nucleation barrier and promoting the crystallisation of HEI phase.

## 4.2.2 Morphological Analysis

The comprehensive morphological characterisation using SEM and transmission electron microscopy (TEM) was hindered by the high beam sensitivity of the particles. Even at low radiation energies in SEM, or during sample preparation for TEM using a focused ion beam (FIB), significant beam-induced damage occurs, leading to material degradation at the observation sites. Gold coating the powders did not alleviate this degradation. Figure 24(a) presents an SEM image of gold-coated HEI-1 powder with minimal focusing time, revealing a surface with substantial roughness and small particles ( $\sim 200$  nm in diameter) protruding. A damaged area caused by the SEM's electron beam is visible on the right side of the image, where perforations are evident. Previous studies on  $\text{MA}_3\text{Bi}_2\text{I}_9$  have reported a porous structure; however, it is likely that the observed porosity resulted from degradation due to electron beam exposure. To mitigate this, the powders were pressed into pellets, allowing for surface analysis using

techniques such as AFM. However, the material's softness complicated AFM imaging, as it tended to stick to the AFM probe. Figure 24(b) and Figure 24(c) show amplitude and amplitude error images of the AFM measurements of the HEI-1 pellet, both indicating a rough surface with growing small particles. Figure 24(d) presents an SEM image of the pressed pellet surface, taken with a short focusing time, which shows a largely uniform, flat morphology. The darker region in the image corresponds to a shadow made during earlier attempts to focus on the surface. The absence of roughness and small particles, compared to the powder morphology, suggests the material undergoes homogeneous plastic deformation when subjected to pressure.

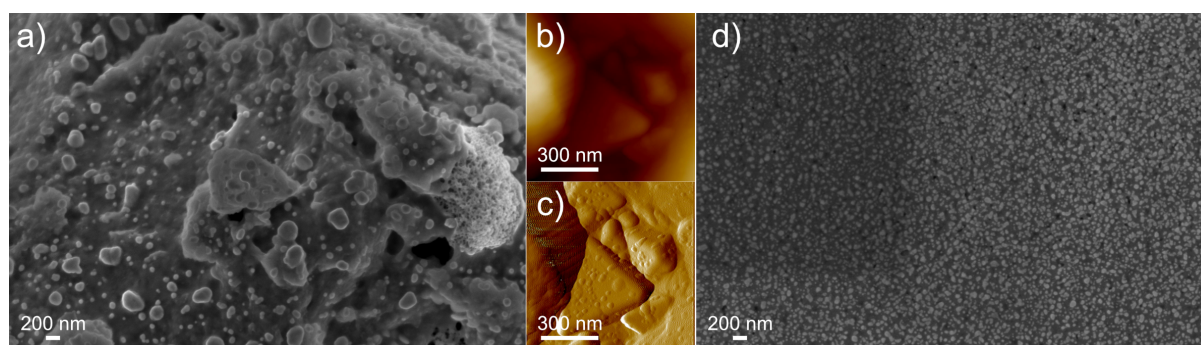


Figure 24: (a) SEM image of gold-coated HEI-1 powder captured at a low accelerating voltage of 5 kV, (b) AFM amplitude, (c) AFM amplitude error, and (d) SEM image of gold-coated HEI-1 pellet.

### 4.2.3 Compositional Analysis

Due to pronounced electron-beam-induced surface degradation, compositional analysis by EDS could not be reliably performed. Figure 25 shows the EDS spectra obtained over a large area at an accelerating voltage of 5 kV. The successful incorporation and distribution of the elements can be seen here; however, the sample was completely burned away by the end of the measurement, raising doubts over the replicability of the results. Therefore, elemental concentrations were instead quantified on powder samples using XRF, with the corresponding results shown in Figure 26. The compositions were obtained by averaging multiple measurements collected across a predefined grid to ensure spatial representativeness. The extracted B-site element ratios fall within the expected equiatomic range, considering experimental uncertainties associated with precursor weighing and minor powder losses during ball milling. These results confirm the successful incorporation of all intended elements into the high-entropy iodide structure.

## Synthesis and Characterisation of Novel High-Entropy Low-Dimensional Perovskite-Derivative Halides

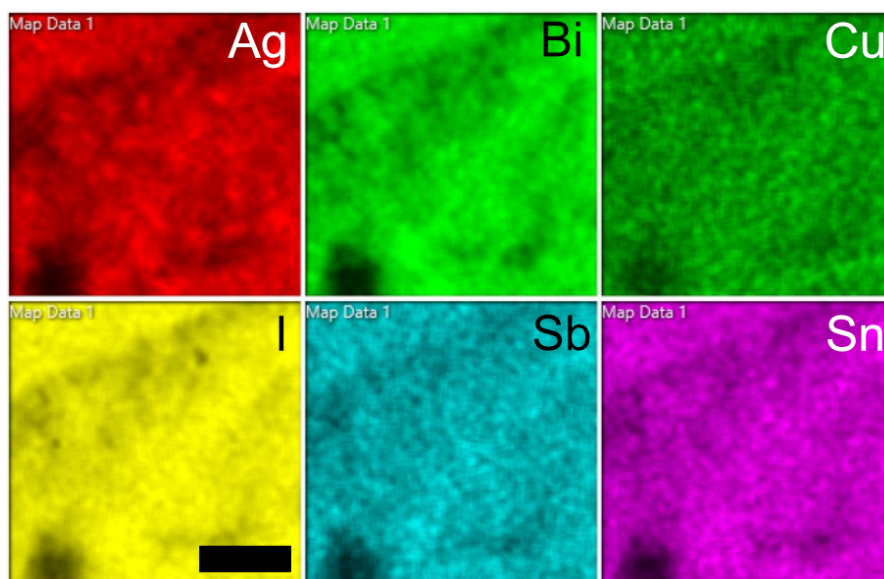


Figure 25: EDS mapping for a gold-coated HEI-1 powder. Scale bar corresponds to 10  $\mu\text{m}$ .

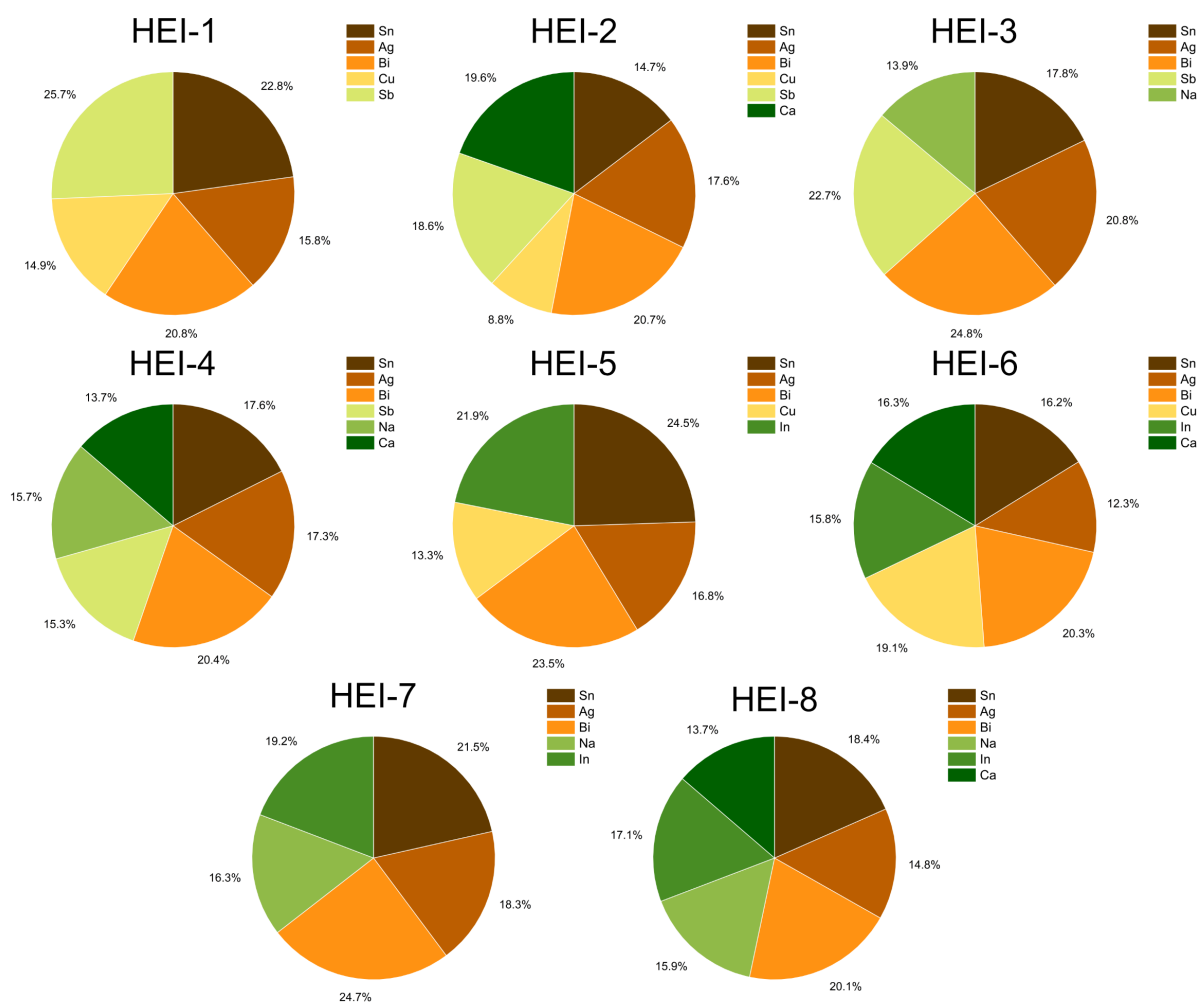


Figure 26: Concentration of B-site elements in the synthesised HEIs from XRF.

#### 4.2.4 Attenuated Total Reflection Infrared Spectrometry

ATR-IR spectroscopy was employed to determine whether the  $(\text{CH}_3\text{NH}_3)^+$  cation remained intact during mechanochemical synthesis or underwent partial decomposition. The characteristic vibrational modes associated with the molecular bonds of the  $(\text{CH}_3\text{NH}_3)^+$  ion were clearly identifiable in the spectra (Figure 27), indicating that the cation was successfully preserved throughout the synthesis. Moreover, the distinct absence of any metal iodide phases in the XRD patterns implies that the  $\text{A}_3\text{B}_2\text{I}_9$  stoichiometry is maintained in the product. Since the A-site can be majorly occupied by  $(\text{CH}_3\text{NH}_3)^+$  amongst the chosen cations, this, combined with the ATR-IR spectroscopy results, indicates that  $(\text{CH}_3\text{NH}_3)^+$  did not undergo significant decomposition during the high-energy synthesis process.

Altogether, the combined spectroscopic and diffraction results demonstrate that all precursor elements are successfully incorporated into the final structure and that the  $(\text{CH}_3\text{NH}_3)^+$  cation remains intact. These findings verify the successful synthesis of multicationic high-entropy iodides, despite their inherent mechanical softness and instability under electron-beam illumination.

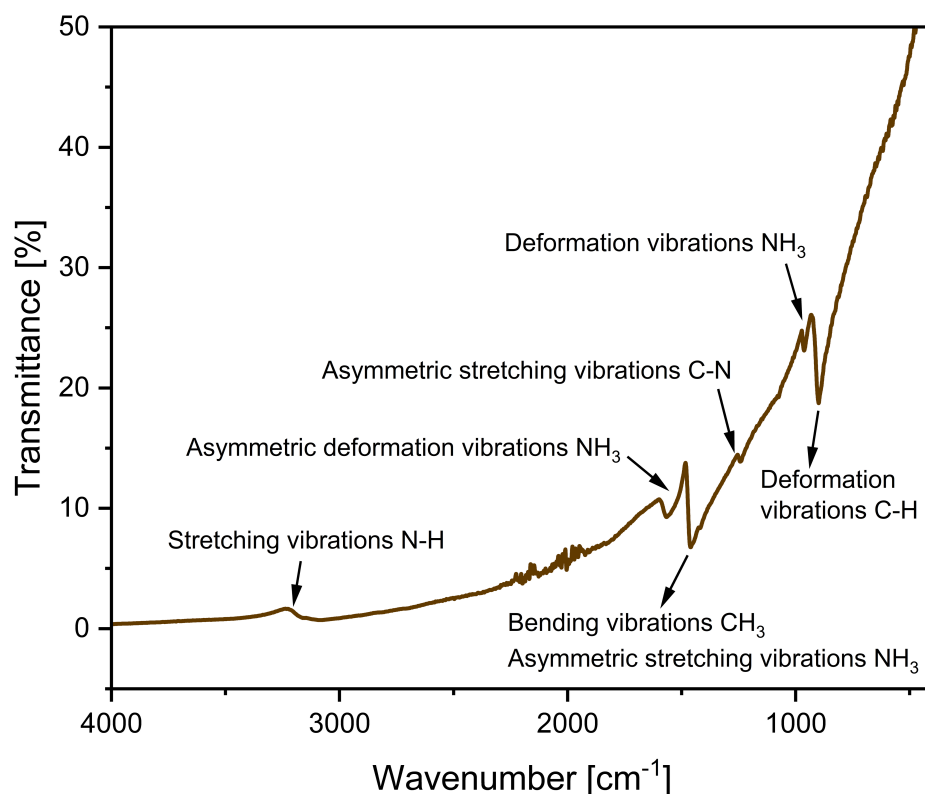


Figure 27: ATR-IR spectra of HEI-1. The typical vibration nodes for  $(\text{CH}_3\text{NH}_3)^+$  can be observed; the asymmetric stretching node for C-N also indicates that the molecule is not completely decomposed during the synthesis.

## 4.2.5 Nanoindentation

During ATR-IR sample preparation and pellet formation for SEM and AFM measurements, HEI-1 exhibited a pronounced pressure-dependent response. Under the compaction pressures applied during pellet pressing, the material behaved in a flux-like manner similar to KBr, indicating that its mechanical properties are strongly altered under load. Individual particles underwent cold flow, plastically deforming to conform to the geometry of the pellet die without fracturing. This behaviour results in the formation of a continuous, glass-like matrix that retains the crystal structure of the starting powders.

To determine whether the mechanical properties of high-entropy iodides depend on their elemental composition, the pellets of the synthesised HEIs were investigated by nanoindentation. Hardness and Young's modulus were determined using an iNano Nanoindenter (KLA) equipped with a Berkovich-shaped diamond tip. Before nanoindentation, the instrument was calibrated using a standard fused silica reference sample. Measurements were performed at room temperature in load control mode with a peak load of 10 mN at a strain rate of  $0.2 \text{ s}^{-1}$  and a dwell time of 10 s at maximum load. For each sample, 20 indentations were conducted, and the results were averaged. Resulting load-depth curves were analysed using the standard Oliver-Pharr method to determine Young's modulus and hardness values.

Typical Young's modulus values reported for perovskites containing organic cations such as  $(\text{CH}_3\text{NH}_3)^+$  range from 1 to 10 GPa.<sup>[145,146]</sup> The measured moduli of synthesised HEIs seem to fall within this range, given in Table 4; however, the results clearly indicate that variations in elemental composition lead to substantial differences in mechanical behaviour. The measurements for HEI-7 seem to be an outlier; however, this can be attributed to its multi-phase nature. Impurity phases might lead to an increase in hardness as they obstruct dislocation propagation or cause inclusion hardening.

*Table 4: Hardness and Young's modulus of the synthesised HEI compositions.*

| Sample | Cationic composition at B-site | Hardness (GPa) | Young's modulus (GPa) |
|--------|--------------------------------|----------------|-----------------------|
| HEI-1  | Sn, Ag, Bi, Cu, Sb             | 0.17           | 9.58                  |
| HEI-2  | Sn, Ag, Bi, Cu, Sb, Ca         | 0.04           | 1.49                  |
| HEI-3  | Sn, Ag, Bi, Na, Sb             | 0.05           | 1.81                  |
| HEI-4  | Sn, Ag, Bi, Na, Sb, Ca         | 0.05           | 1.99                  |
| HEI-5  | Sn, Ag, Bi, Cu, In             | 0.12           | 4.85                  |
| HEI-6  | Sn, Ag, Bi, Cu, In, Ca         | 0.03           | 1.05                  |



|       |                        |      |       |
|-------|------------------------|------|-------|
| HEI-7 | Sn, Ag, Bi, Na, In     | 0.38 | 22.33 |
| HEI-8 | Sn, Ag, Bi, Na, In, Ca | 0.07 | 2.75  |

HEI-1 exhibits the highest stiffness and hardness ( $E = 9.58$  GPa;  $H = 0.17$  GPa), reflecting a comparatively rigid lattice with a higher resistance to plastic deformation and a more brittle mechanical response, with HEI-5 having a comparatively moderate hardness. In contrast, HEI-2, HEI-3, HEI-4, HEI-6, and HEI-8 exhibit significantly lower Young's moduli (below 3 GPa) and hardness values (below 0.07 GPa), indicating a much softer mechanical character. These reduced mechanical resistances facilitate local deformation, creep, and even macroscopic flow under moderate pressure, phenomena commonly observed in soft ionic solids.

The marked differences in stiffness ( $\sim 9.6$  vs.  $\sim 1$  GPa) can be attributed to variations in charge distribution, ionic size mismatch, and lattice distortions that reduce bonding strength. In halide perovskites, the incorporation of smaller cations generally increases lattice rigidity due to compression effects.<sup>[147,148]</sup> In the present case, the primary compositional distinction is the presence or absence of  $\text{Ca}^{2+}$  or  $\text{Na}^+$ . The highest hardness is observed in the composition lacking both  $\text{Ca}^{2+}$  and  $\text{Na}^+$  (HEI-1 and HEI-5), suggesting that their incorporation softens the lattice. Although the detailed mechanism remains to be fully resolved,  $\text{Ca}^{2+}$  and  $\text{Na}^+$  likely weaken electrostatic interactions, as alkali and alkaline-earth cations promote more ionic, less covalent bonding due to the absence of d-orbital participation. In their absence, the lattice may retain a higher degree of covalency, contributing to enhanced rigidity.

Furthermore, the inclusion of  $\text{Ca}^{2+}$  or  $\text{Na}^+$  necessitates additional charge compensation to maintain an average cationic charge of 3+, thereby perturbing the local coordination environment. In the case of HEI-1,  $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.2}\text{Ag}_{0.2}\text{Bi}_{0.2}\text{Cu}_{0.2}\text{Sb}_{0.2})_2\text{I}_9$ , and HEI-5,  $(\text{CH}_3\text{NH}_3)_3(\text{Sn}_{0.2}\text{Ag}_{0.2}\text{Bi}_{0.2}\text{Cu}_{0.2}\text{In}_{0.2})_2\text{I}_9$ , elements such as Sb, Sn, Bi, and In are present, which can adopt higher oxidation states and help stabilise a stiffer lattice. On the contrary, in HEI-2, HEI-3, HEI-4, HEI-6, and HEI-8, the incorporation of  $\text{Ca}^{2+}$  or  $\text{Na}^+$  introduces lower-charge species that require compensation, increasing lattice distortions and weakening bonding interactions. These combined effects yield a more compliant and less cohesive lattice, consistent with the markedly lower moduli observed for these systems. Increased ionic character may also elevate iodine migration barriers, potentially reducing ionic mobility.<sup>[149]</sup>

Overall, these findings show that the mechanical behaviour of high-entropy iodides can be systematically tuned through cation selection. Transition-metal and semimetal cations (Sn, Sb, Bi, and In) reinforce the lattice, whereas alkali-group cations (Na, Ca) substantially reduce stiffness. This establishes a clear design principle linking

composition to mechanical compliance and positions the compositions without Na or Ca as model soft ionic solids with pronounced flow behaviour comparable to classical compounds such as KBr, but with the added complexity and tunability inherent to high-entropy chemistry.

## 4.3 Optoelectronic Characterisation

As these materials are intended to be used as absorber materials for photovoltaics, comprehensive optoelectronic characterisations provide insight into their band structures and charge carrier behaviour.

### 4.3.1 UV-Vis Spectroscopy

Absorbance measurements were performed on a UV-Vis-NIR spectrometer (Cary 5000, Agilent) with a double-beam setup. Spin-coated thin films were used for measurements in the transmission mode.

First, to optimise film quality, different combinations of solvents, spin-coating parameters, and annealing conditions were evaluated for HEI-1. Table 5 lists the combinations that resulted in viable films. The solvent mixture of DMF and NMP in a 1:1 (v/v) ratio, along with spin-coating at 3000 RPM for 30 s, resulted in a film with the highest absorbance (shown in Figure 28), after annealing directly on a hot plate after spin-coating. These parameters were used for preparing thin films for all compositions.

*Table 5: Solvent, spin-coating parameters, and annealing conditions used for preparing thin films of HEI-1.*

| Sample name | Solvent             | Spincoating parameters | Annealing conditions    |
|-------------|---------------------|------------------------|-------------------------|
| TF-1        | DMF:NMP; 1:1 (v/v)  | 3000 RPM; 30 s         | Direct on hot plate     |
| TF-2        | DMF:NMP; 1:1 (v/v)  | 4000 RPM; 30 s         | Vacuum 30 s → hot plate |
| TF-3        | DMF                 | 3000 RPM; 30 s         | Direct on hot plate     |
| TF-4        | DMF                 | 4000 RPM; 30 s         | Vacuum 30 s → hot plate |
| TF-5        | DMSO:DMF; 1:1 (v/v) | 3000 RPM; 45 s         | Direct on hot plate     |
| TF-6        | DMSO:NMP; 1:1 (v/v) | 4000 RPM; 45 s         | Vacuum 30 s → hot plate |
| TF-7        | DMSO                | 3000 RPM; 45 s         | Direct on hot plate     |



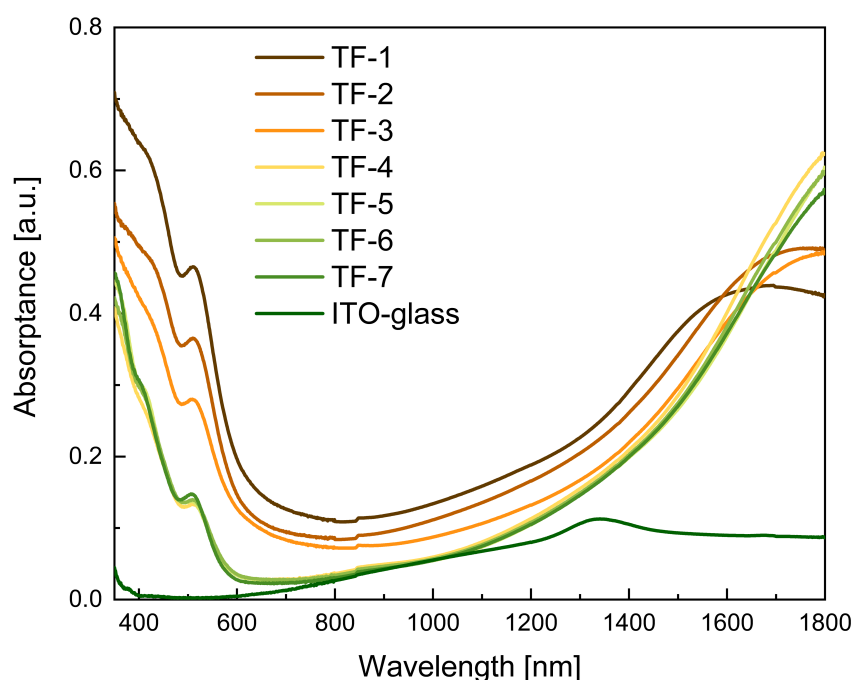


Figure 28: Comparison between absorbance measurements of HEI-1 thin films prepared using different parameters.

The absorbance of all the prepared HEIs is shown in Figure 29(a). Barring HEI-7, all other compositions have an absorption edge between 550 and 600 nm. The anomalous behaviour of HEI-7 can be attributed to the impurity phases present in the system. Figure 29(b) and Figure 29(c) illustrate the Tauc plots corresponding to the direct and indirect allowed transitions, respectively. The direct band gaps range between 1.95 and 2.11 eV (excluding HEI-7), and the indirect band gaps between 0.97 and 1.58 eV. The Tauc plots for the direct transitions exhibit a steeper linear increase near the onset of the absorption edge, suggesting that the HEIs are direct band gap semiconductors. Previous reports on low-dimensional  $\text{MA}_3\text{Bi}_2\text{I}_9$  have already indicated that it exhibits a direct band gap, which is consistent with the observations presented here.<sup>[96,150,151]</sup> The dark-red visual appearance also corresponds with the measured optical band gap of around 2 eV for these compounds. A strong, broad excitonic absorption feature appears around 480 nm (corresponding to an energy of 2.48 eV), which can be attributed to the  $^1\text{S}_0 \rightarrow ^3\text{P}_1$  electron transition associated with  $\text{Bi}^{3+}$  ions in the face-shared  $[\text{Bi}_2\text{I}_9]^{3-}$  dioctahedral units.<sup>[138]</sup> A similar transition could also be possible for the other trivalent cations in the HEI systems.

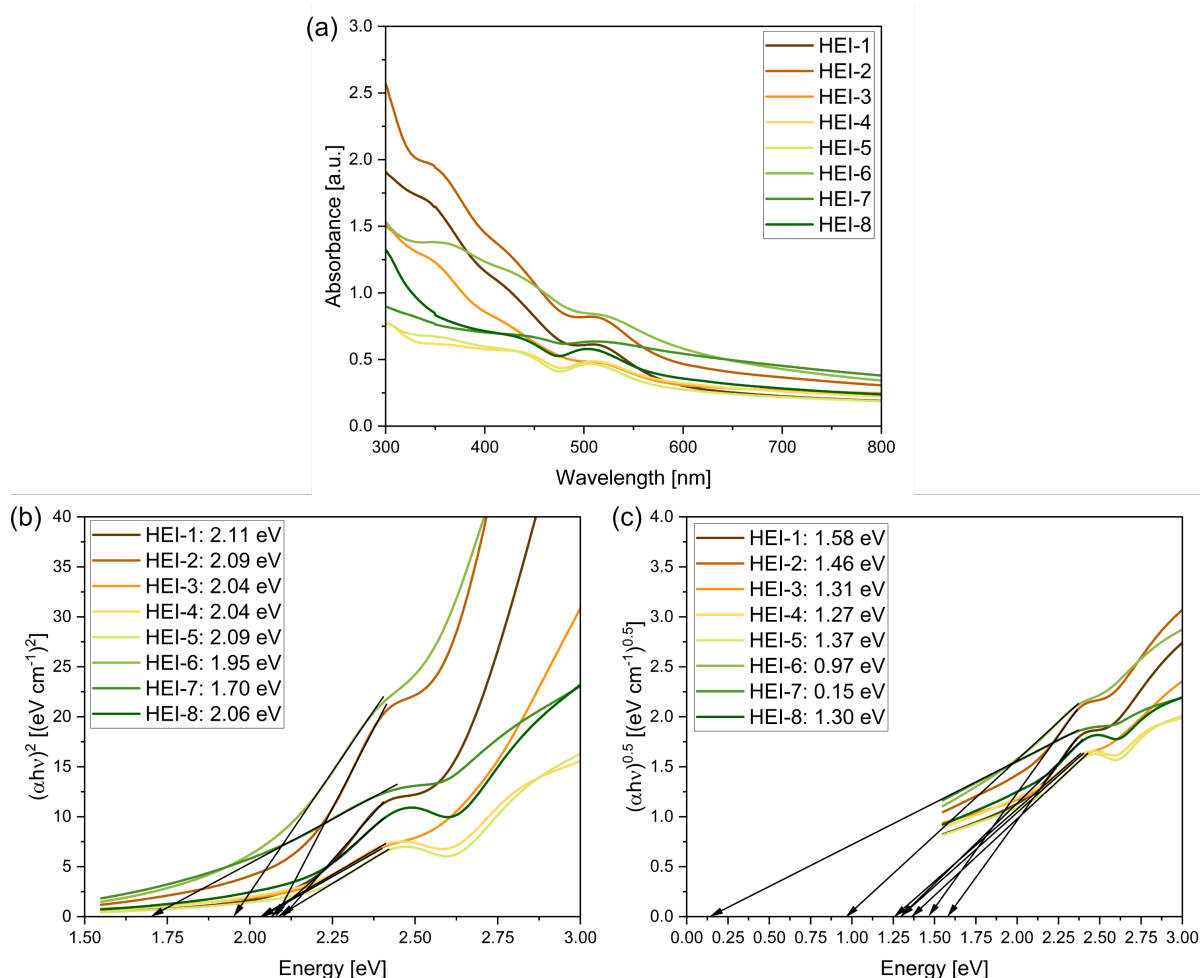


Figure 29: (a) UV-Vis absorbance for prepared HEI thin films, (b) and (c) Tauc-plot fits indicating direct and indirect band gaps for the HEI films, respectively.

The direct band gaps for all the HEI compositions are in a relatively narrow range, taking any discrepancies due to fitting error into account, despite the differing elemental compositions. Compositional changes, along with varying degrees of crystallinity, make it unusual that only such negligible differences appear. Previous reports on MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> derivatives have found direct band gaps ranging between 2.1 and 2.4 eV.<sup>[96,150,152]</sup>

Usually, low-dimensional perovskite derivatives like MA<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> exhibit an indirect band gap in the range 2-2.3 eV. The [Bi<sub>2</sub>I<sub>9</sub>]<sup>3-</sup> clusters localise electronic states and favour indirect transitions. This change from an indirect to a direct band gap observed in HEIs may arise due to structural modifications like reduced inter-cluster spacing and lattice contractions, or increased orbital overlaps.

This implies that the high-entropy approach has a considerable effect on the crystal formation and its mechanical properties; the effect on the band gap is not as significant. The slight reduction in band gaps may arise from distortions in the band structure resulting from the intricate local electronic environment created by the diverse cations and defect states. These complex bonding interactions have been shown to alter the

density of states near the Fermi level for other high-entropy systems.<sup>[149]</sup> The change in the associated electronic structure would also influence the charge carrier dynamics and the optical properties.<sup>[152]</sup> The creation of defect states due to the inclusion of a variety of cationic species would create new pathways for carrier excitation and recombination, thereby hampering their capabilities as an absorber material.

### 4.3.2 Photoelectron Spectroscopy in Air

PESA was used to determine the ionisation energies of the semiconductors using an AC-2E photoelectron spectrometer (Riken Keiki) on pressed pellets, with all measurements referenced to  $\text{MA}_2(\text{AgBi})\text{I}_6$ .<sup>[153]</sup> Figure 30 depicts the measured photoelectron intensities for  $\text{MA}_2(\text{AgBi})\text{I}_6$  and HEI-1. Extracting the ionisation energies from linear fits to the PESA onset yielded values of 5.64 eV for  $\text{MA}_2(\text{AgBi})\text{I}_6$  and significantly lower values for the HEI compositions, indicating notable differences in their electronic structures or densities of states. A further distinction emerged from the markedly different excitation conditions required to obtain comparable signal intensities:  $\text{MA}_2(\text{AgBi})\text{I}_6$  required approximately 100-fold higher UV power than the HEI compositions (1000 vs. 10 nW). Given that both samples were prepared using the same synthesis route, it is assumed that similar surface conditions exist. The substantially lower photoelectron quantum efficiency of  $\text{MA}_2(\text{AgBi})\text{I}_6$  may therefore stem from reduced optical absorption or a lower density of occupied electronic states contributing to photoemission. Conversely, in the case of HEI-1, its multicomponent nature may enhance the density of occupied states near the valence-band maximum, enabling more efficient photoelectron emission. These increases may arise due to vacancies created by the variation of oxidation states across the cationic space, resulting in occupied defect states within the band gap. These compensating defects would shift the Fermi level and alter band bending, thereby changing the apparent ionisation potential, rather than causing a large shift in the bulk band edge, as there is no orbital reordering. The observed downward shift may also reflect a variation in orbital character due to the inclusion of a multitude of cations, i.e., a reduction in the contribution of  $ns^2$  states towards the valence edge; however, this effect is usually not as pronounced.<sup>[154]</sup>

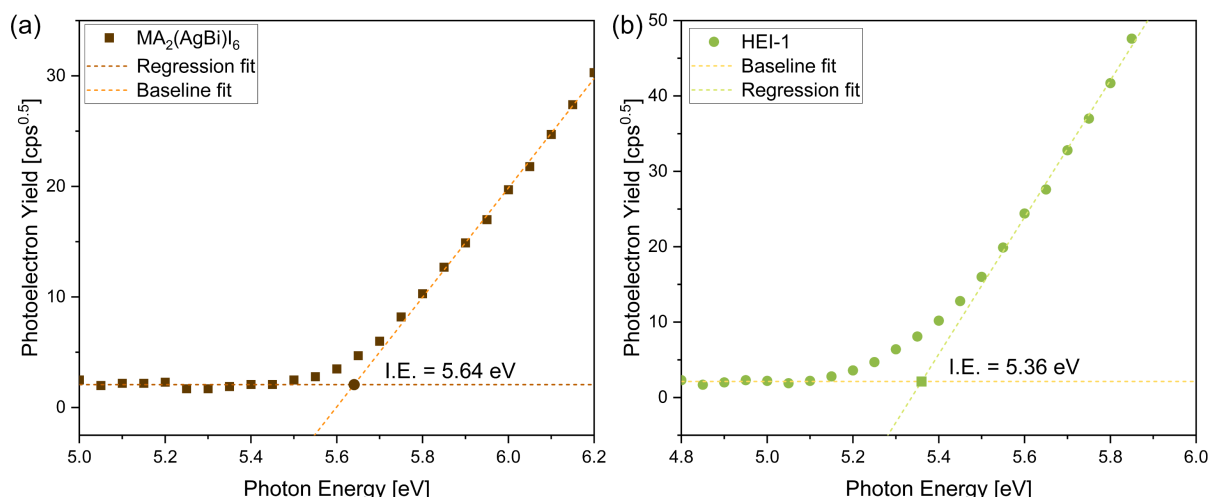


Figure 30: (a) and (b) PESA measurements indicate ionisation energies of 5.64 eV and 5.36 eV for MA<sub>2</sub>(AgBi)I<sub>6</sub> and HEI-1, respectively.

### 4.3.3 Photoluminescence Spectroscopy

PL spectroscopy was attempted on HEI powder and thin-film samples. However, the thermal effects from the incident laser cause the samples to melt, making it impossible to collect an accurate PL spectrum.

### 4.3.4 Solar Cell Performance

Finally, to assess the applicability of the synthesised HEIs as solar cell absorber materials, solar simulation measurements were carried out on prepared solar cell stacks with assistance from [Holger Röhm](#). The JV curves of the solar cells were measured in an inert atmosphere using a Keithley source measurement unit, both in the dark and under illumination from a solar simulator (Sciencetech Lightline, Air Mass (AM) 1.5, 1000 W m<sup>-2</sup>, calibrated with a Si reference solar cell). The scan speed in reverse (1.2 V → -0.4 V) direction was 200 mV s<sup>-1</sup>.

The reference solar cells prepared using MAPbI<sub>3</sub> as the absorber layer achieved a maximum efficiency of 11.53% with a FF of 72.35%, demonstrating that the fabrication process yields operational solar cells. However, the best performing solar cell where HEI-1 was used as the absorber material achieved an efficiency of 0.000812% with a FF of 27.25%. While the FF is poor, it does not explain the exceedingly poor efficiencies alone. The low J<sub>SC</sub> of 73 μA cm<sup>-2</sup> also suggests very weak photocurrent generation, indicating severe recombination within the absorber layer. Such behaviour could be caused by a variety of reasons, including unoptimized deposition, pinholes within the film, mismatched energy layers creating interfacial barriers, or poor electrode interfaces.

## 4.4 Conclusion

In this work, the first demonstration of low-dimensional, perovskite-derived high-entropy iodides has been successfully achieved, thereby extending the high-entropy design paradigm into the realm of iodide-based perovskites.

Mechanochemical synthesis has been utilised for the formation of  $\text{MA}_3\text{Bi}_2\text{I}_9$ -based HEIs, where the B-site has been substituted by a mixture of cations chosen from Sn, Ag, Bi, Cu, Sb, Na, In, and Ca, though only under high milling energies and extended durations, underscoring the fine balance between entropy-driven cation mixing and crystallographic stability. Combined crystallographic and compositional analyses confirm the complete incorporation of the precursor elements and retention of the  $(\text{CH}_3\text{NH}_3)^+$  cation, corroborating the successful synthesis of multi-cationic HEIs.

These HEIs behave similarly to soft ionic compounds, such as KBr, under the application of mechanical load. Their Young's modulus and hardness vary by more than an order of magnitude depending on the incorporated cations. Transition-metal and semimetal species (Sn, Sb, Bi, and In) strengthen the lattice, while alkali-group cations (Na and Ca) significantly soften it, establishing a clear composition–mechanics design principle.

All the dark red HEIs exhibit a direct band gap confined to a narrow range (1.9–2.1 eV), which can be subtly adjusted through compositional choice, enabling predictable optoelectronic behaviour. Corresponding shifts in electronic structure due to the presence of a complex cationic space and inclusion of associated defects also suggest opportunities to tune ionisation energy and the distribution of occupied states. However, their value as solar cell absorbers still leaves much to be desired. Further improvements in film quality and device structure are required to fully realise their potential.

Together, these results demonstrate that high-entropy iodides combine robust, composition-tunable optical characteristics and highly adjustable mechanical properties, positioning them as a versatile new materials platform. Their distinctive structure–property relationships may support tailored applications in photodetectors, solid-state ionics, and flexible optoelectronic coatings. Future work should aim to directly link entropy-induced lattice distortions to charge-carrier dynamics and long-term stability, ultimately guiding the development of functional HEI-based devices.



## 5 Development of High-Entropy Perovskite Oxides for Use as Absorber Layers in Solar Cells

As previously mentioned, the commercial deployment of lead-based photovoltaic devices faces significant barriers, including the toxicity of lead and the inherent instability of lead halides in the face of environmental degradation. As global acceptance of solar energy increases, sustainable and environmentally safe materials are needed to meet both technological and regulatory requirements. Oxide-based semiconductors, in contrast, present a promising foundation for sustainable solar cell absorbers. Metal oxides are intrinsically robust, exhibit excellent resistance to environmental degradation, have a low ecological footprint, and are well-established in large-scale industrial processing. These attributes make them attractive for future photovoltaic devices designed for long operational lifetimes and minimal environmental impact.

However, when oxide-based semiconductors are considered as absorber materials, they face challenges due to their intrinsic material properties. They generally have wide band gaps, which restrict absorption across the entire solar spectrum, resulting in low photocurrent generation. As defect states due to oxygen vacancies or cation deficiencies are extremely widespread, there is a higher rate of electron-hole recombination, which also reduces their photovoltaic efficiency. Charge transport through polaronic conduction also reduces charge-carrier mobilities, resulting in reduced charge extraction from the absorber layer.

HEPOs present themselves as an attractive alternative given their ability to tailor properties and drastically change the electronic landscape from the unique interactions between the multitude of cations within the lattice.<sup>[68,155]</sup> A smaller optical absorption edge can be engineered through the judicious selection of constituent cations, thereby helping reduce the wider band gaps of oxides and improving the absorption within the solar spectrum.<sup>[52,156]</sup> The defect formation energies are also modified because of the entropic stabilisation in such systems, which can be utilised to reduce the concentration of deep trap states or passivate them, helping lower the rate of electron-hole recombination, which plagues oxide semiconductors.<sup>[157]</sup> The distorted lattices of HEPOs are also highly resistant to structural and chemical degradation, which could help increase the operational lifetimes of photovoltaic devices constructed using them.<sup>[158]</sup> The immense possibilities materialising through HEPOs may hold the key to finding stable lead-free alternatives for use as absorber layers.

This chapter explores the synthesis and characterisation of different types of HEPOs using various synthesis routes. A key reason behind investigating HEPOs for this application was that ferroelectric behaviour helped enhance the efficiency of lead-halide PSCs due to improved charge-carrier separation.<sup>[159]</sup> It is believed that the highly distorted

structures obtained within these compositionally complex systems might help improve their inherent ferroelectric behaviour. The goal of this work is to engineer an all-oxide solar cell using solution-processable routes, wherein both the absorber and charge transport layers are constructed from environmentally friendly, scalable, and highly stable oxide materials.

## 5.1 Materials Synthesis

### 5.1.1 Powder Preparation

#### 5.1.1.1 Lanthanum-Based Perovskite Oxides

The majority of this work focused on derivatives based on the  $\text{LaBO}_3$  structure. La-based perovskite systems, such as  $\text{LaNiMnO}_6$ ,  $\text{LaFe}_{0.9}\text{Zn}_{0.1}\text{O}_3$ , and  $\text{LaMnO}_3$ , have been explored as absorber layers for solar cells due to their smaller band gaps ( $\sim 1.6\text{--}1.8$  eV), which show good ambient stability and light absorption.<sup>[160–162]</sup> The high-entropy approach is being applied to them to further reduce the bandgap and enhance electrical conductivity. Fourteen compositions (listed in Table 6) based on lanthanum perovskites were synthesised using a mixture of five different transition metals, chosen from Cr, Mn, Fe, Co, Ni, Cu, and Zn, occupying the B-site lattice positions in the perovskite structure. To investigate their suitability for optical applications, we sought to tune their band structure by varying the B-site composition, since the B-site cation significantly influences the electronic properties of a perovskite and plays a crucial role in determining its band gap.<sup>[163]</sup> The transition metals were selected for this study because they all possess similar ionic radii, which minimises the risk of phase separation during synthesis. In addition, most of them also form binary or ternary perovskites with La. Since these selected transition metals can exhibit multiple valence states, charge neutrality can be maintained in the event of vacancy generation. All these factors together support the formation of a single-phase high-entropy oxide.<sup>[164]</sup>

A modified Pechini process was used for the synthesis of the HEPOs, as it has been previously employed for the synthesis of other HEOs.  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , were used as the precursors for the incorporating cations into the system as nitrate salts are highly soluble in water. These precursor nitrates were dissolved in distilled water in stoichiometric ratios for each composition under constant stirring until a homogeneous solution was obtained. Citric acid (CA) was used as a chelating agent, and ethylene glycol (EG) was used to promote esterification of the citrate complexes. These two were then added to the above solutions in a predetermined molar ratio, metal cations: CA: EG = 1:1:4, to form metal-citrate complexes, while maintaining the solution at 80 °C under continuous stirring for  $\sim 1$  hour until a homogeneous solution was obtained. This prepared solution was then heated to 150 °C and maintained at that temperature for  $\sim 2$  hours to induce the esterification of CA with the aid of EG, creating a



polyester network. The metal-citrate complexes were trapped within this network, helping maintain a homogeneous distribution of cations. Water is evaporated from the system on continued heating, resulting in the formation of a black viscous gel. Afterwards, the gel was pyrolysed at 300 °C to ensure the removal of any unreacted organic precursors and moisture, which could cause spillage issues during the calcination at higher temperatures, until a dried ashy foam was obtained containing intermediate metal oxides and organic complexes. The dried foam thus obtained was then ground using an agate mortar and pestle for 10 min to ensure the final product has a homogeneous particle size distribution. The ground-up gel was then calcined at 1200 °C in a furnace with an air atmosphere, followed by slow-cooling in the furnace to obtain fine powders of the desired HEPO composition.

*Table 6: Compositions of the synthesised samples based on transition metal lanthanide perovskites.*

| Sample name | Composition                  | Sample name | Composition                  |
|-------------|------------------------------|-------------|------------------------------|
| PS-1        | La(CoCrCuFeMn)O <sub>3</sub> | PS-8        | La(CoCrFeNiZn)O <sub>3</sub> |
| PS-2        | La(CoCrFeMnZn)O <sub>3</sub> | PS-9        | La(CoCuFeMnNi)O <sub>3</sub> |
| PS-3        | La(CrCuFeMnNi)O <sub>3</sub> | PS-10       | La(CoFeMnNiZn)O <sub>3</sub> |
| PS-4        | La(CrFeMnNiZn)O <sub>3</sub> | PS-11       | La(CrCuFeMnZn)O <sub>3</sub> |
| PS-5        | La(CoCrCuMnNi)O <sub>3</sub> | PS-12       | La(CrCuMnNiZn)O <sub>3</sub> |
| PS-6        | La(CoCrMnNiZn)O <sub>3</sub> | PS-13       | La(CoCrCuNiZn)O <sub>3</sub> |
| PS-7        | La(CoCrCuFeNi)O <sub>3</sub> | PS-14       | La(CoCuFeNiZn)O <sub>3</sub> |

Higher calcination temperatures are required for the synthesis of these perovskites compared to other HEOs, as the Jahn-Teller (JT) distortions arising from the inclusion of Mn or Cu in the system often hamper the formation of a single phase.<sup>[165]</sup> The JT distortions are favourable at lower temperatures, resulting in the stabilisation of lower-symmetry, more distorted lattices that exhibit multiple phases. Relaxation to symmetric perovskite structures is achieved only at elevated temperatures, where the effects from JT distortions are reduced, and the perovskite structures are more thermally stable.<sup>[166]</sup>

The structural stability of perovskites can also be predicted using geometric factors as mentioned in Section 2.2.1. Based on the elemental compositions of the chosen systems, the Goldschmidt tolerance factor ( $t$ ), octahedral factor ( $\mu$ ), and the oxidation tolerance factor ( $\tau$ ) have been tabulated in Table 7. The Shannon radii of the transition metals were used to calculate the average cationic radii of the B-site. Since  $0.9 < t <$

1,  $0.414 \leq \mu \leq 0.732$ , and  $\tau < 4.18$  for all compositions, we can postulate that a perovskite should be possible for them, as explained earlier in Section 2.2.1.

*Table 7: The tolerance factor, octahedral factor, and the oxidation state-weighted tolerance factor for the proposed compositions.*

| Sample name | Tolerance factor ( $t$ ) | Octahedral factor ( $\mu$ ) | Oxidation tolerance factor ( $\tau$ ) |
|-------------|--------------------------|-----------------------------|---------------------------------------|
| PS-1        | 0.970                    | 0.436                       | 1.6855931                             |
| PS-2        | 0.952                    | 0.465                       | 1.68814576                            |
| PS-3        | 0.971                    | 0.435                       | 1.68321103                            |
| PS-4        | 0.952                    | 0.464                       | 1.6855931                             |
| PS-5        | 0.975                    | 0.43                        | 1.67621681                            |
| PS-6        | 0.956                    | 0.459                       | 1.67800201                            |
| PS-7        | 0.975                    | 0.43                        | 1.67621681                            |
| PS-8        | 0.956                    | 0.459                       | 1.67800201                            |
| PS-9        | 0.972                    | 0.434                       | 1.68208396                            |
| PS-10       | 0.953                    | 0.463                       | 1.68438074                            |
| PS-11       | 0.958                    | 0.455                       | 1.73212482                            |
| PS-12       | 0.962                    | 0.449                       | 1.71273789                            |
| PS-13       | 0.966                    | 0.444                       | 1.70006398                            |
| PS-14       | 0.963                    | 0.448                       | 1.71079876                            |

#### 5.1.1.2 Derivatives of Barium Titanate

Other compositions based on different perovskites were also synthesised within the scope of this thesis, which are tabulated below (Table 8). For some of these samples, reverse co-precipitation and solid-state synthesis were also attempted to observe any variation in phase formation. Metal nitrate precursors were used for most cations, barring titanium (titanium n-butoxide), niobium (ammonium niobate oxalate hydrate), and vanadium (vanadium chloride) for reverse co-precipitation. In compositions where Ba is present, ethylenediaminetetraacetic acid (EDTA) was used as a chelating agent, as it works better in basic conditions compared to citric acid, and  $\text{Ba}(\text{NO}_3)_2$  requires a basic environment for higher solubility. Reverse co-precipitation was performed using

ammonia as the precipitating agent, with titration conducted under constant stirring to ensure homogeneous precipitate size. For solid-state synthesis, the metal oxides of the desired components were used as precursors. These oxides were mixed thoroughly using a mortar and pestle and then calcined in air at 1000 °C to form the HEPOs.

### 5.1.1.3 Derivatives of Potassium Niobate

KNBNNO,  $(K_{0.5}Na_{0.5})NbO_3$  (KNN) doped with 2 mol%  $Ba(Ni_{0.5}Nb_{0.5})O_{3-\delta}$  (BNNO), has been proven to be a multifunctional perovskite phase with excellent ferroelectric and optical properties. Thus, a high-entropy approach was used to further improve the response of this material in the development of an oxide solar absorber, with the composition  $(Li_{0.1}Na_{0.1}K_{0.2}Ca_{0.2}Sr_{0.2}Ba_{0.2})(Nb_{0.95}Ni_{0.05})O_3$ .

Table 8: Other perovskite compositions, not based on lanthanum perovskites.

| Composition                                        | Comments                                                                                                                                                                                                                 |
|----------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $Sr(CeNbSnYZr)O_3$                                 | Band gap engineering of $SrZrO_3$ can help reduce it to optimal ranges for photovoltaic applications. Theoretical studies have shown small effective charge carrier masses pointing to efficient conversion.             |
| $(BaCaKLi_{0.5}Na_{0.5}Sr)(Ti_{0.95}Ni_{0.05})O_3$ | $(K_{0.5}Na_{0.5})NbO_3$ – $BaNi_{0.5}Nb_{0.5}O_{3-\delta}$ has a band gap of 1.39 eV. Modifications to improve its photocurrent generation would make it an ideal oxide alternative as an absorber material.            |
| $(BaCaKLi_{0.5}Na_{0.5}Sr)(Nb_{0.95}Ni_{0.05})O_3$ |                                                                                                                                                                                                                          |
| $Ba(CrFeMnNbTi)O_3$                                | $BaTiO_3$ is a well-studied ferroelectric material with a wide band gap. Engineering this towards lower can provide pathways for optoelectronic applications.                                                            |
| $Ba(CeNbTiYZr)O_3$                                 |                                                                                                                                                                                                                          |
| $Bi(CrFeMnNiTi)O_3$                                | $BiFeO_3$ perovskites have been studied as absorber materials due to their ferroelectric properties and low band gap (~2 eV). Improvement in photocurrent generation is the biggest hurdle towards further applications. |
| $Bi(CrFeMnNiV)O_3$                                 |                                                                                                                                                                                                                          |

## 5.1.2 Thin Film Preparation

As the final goal of this work is to develop solution-processable solar cell stacks, thin-film deposition is a crucial prerequisite. For oxides, the most common way to prepare thin films is through spin-coating or printing nanoparticle dispersions. However, such particulate thin films exhibit a significantly lower PCE compared to continuous crystalline films. These reductions stem from non-radiative recombination losses at the surface and interface traps, as well as reduced charge carrier mobilities due to the interparticle boundaries. Since oxide absorbers aren't very efficient to begin with, it is of utmost importance that a continuous crystalline film be used within solar cell stacks.

As the  $\text{LaBO}_3$ -type HEPOs show the most potential as absorber materials for the solar cells, the thin film deposition was focused on them. The modified Pechini process used for their synthesis can also be adapted to prepare thin films.<sup>[24]</sup> The same metal nitrate precursors used for their powder preparation were also employed to make thin films of these HEPOs. They were dissolved in a stoichiometric ratio to make a 0.1 M solution. 2-methoxyethanol was used as the solvent due to its superior viscosity and wettability on substrates compared to water. CA and EG were added to this mixture in a predetermined molar ratio, metal cations: CA: EG = 1:1:2, while the solution is kept at 80 °C under constant stirring. This stirring is allowed to continue until the volume of the solution has reduced considerably, and the viscosity has increased enough that it leaves a thin coating along the walls of the beaker when shaken. This solution is then allowed to age overnight to ensure complete chelation of the metal cations has taken place. The solution is ready for spin-coating after this ageing step. Sapphire substrates were used for thin film deposition, as they can withstand the higher calcination temperatures required for the synthesis of these HEPOs. The substrates were cleaned ultrasonically in water, isopropanol, and acetone. They were then treated with oxygen plasma for 2 minutes to improve their wettability. 40  $\mu\text{l}$  of the prepared solution was deposited on the substrates before spin coating at 3000 rpm for 30 seconds. The films were then annealed in an air atmosphere furnace at 1200 °C for 4 hours, with a ramping rate of 5 °C  $\text{min}^{-1}$ .

## 5.2 Structural and Compositional Characterisation

### 5.2.1 Crystallographic Analysis

#### 5.2.1.1 Powder Analysis for $\text{LaBO}_3$ -type Perovskites

In  $\text{ABO}_3$  perovskites, a smaller A-site cation creates a preference for the crystallisation of an orthorhombic or a rhombohedral crystal structure. This can be seen in the case of the parent lanthanum perovskite oxides of transition metals, which demonstrate either an orthorhombic structure ( $Pnma$ ; for  $\text{LaCrO}_3$ ,  $\text{LaMnO}_3$ , and  $\text{LaFeO}_3$ ) or a rhombohedral structure ( $R-3cH$ ; for  $\text{LaNiO}_3$ ,  $\text{LaCoO}_3$ , and  $\text{LaCuO}_3$ ).  $\text{LaZnO}_3$  stands out as an outlier with a hexagonal structure ( $P63mc$ ). Figure 31 gives a visualisation of the various structures possible for lanthanum perovskite oxides.

The crystal structures of the synthesised HEOs were characterised using XRD measurements performed with a  $\text{Cu-K}\alpha_{1,2}$  source in the 10°–90° range using the Bragg-Brentano geometry. Rietveld refinement of these patterns was then carried out using the Profex 5.5.0 software. The refinement was carried out by modifying the elemental composition according to the respective sample for the lanthanum-based HEPOs, utilising the reference structures of  $\text{LaCrO}_3$  (space group  $Pnma$ , code 70544) and  $\text{LaCuO}_3$  (space group  $R-3cH$ , code 9428), taken from the ICSD database. The instrumental intensity distribution was determined by employing a reference scan of SRM-1976b (strain-free  $\text{Al}_2\text{O}_3$  in a glassy matrix with a particle size >2  $\mu\text{m}$ ).

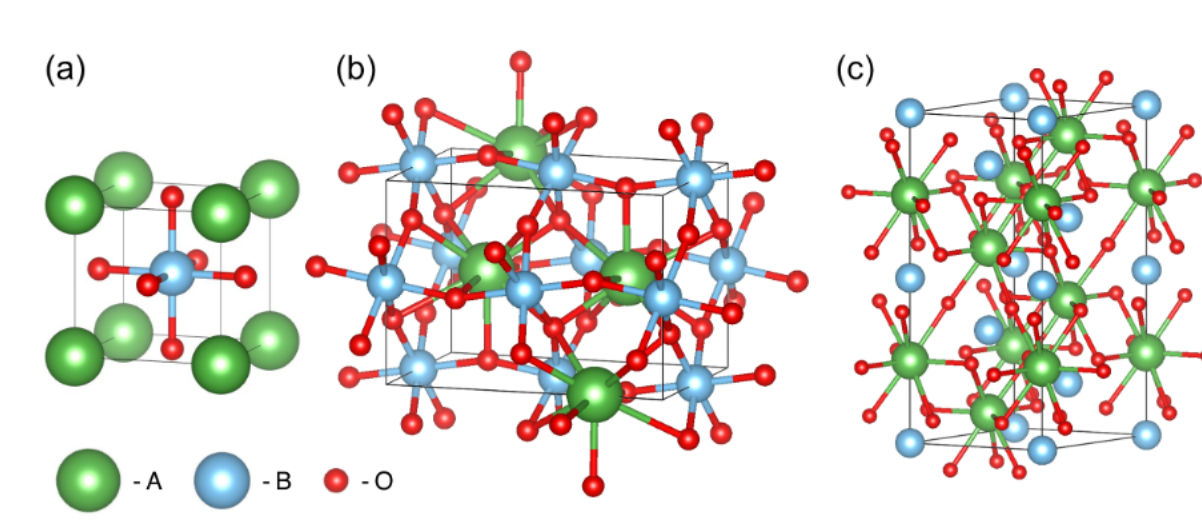


Figure 31: (a) Crystal structure unit cell of an ideal cubic perovskite,  $ABO_3$ . (b) The crystal structure of a perovskite oxide with an orthorhombic structure, like  $LaCrO_3$ . (c) The crystal structure of a perovskite oxide with a rhombohedral structure, like  $LaCuO_3$ . Figures created using Vesta.<sup>[142]</sup>

The XRD patterns for the lanthanum-based HEPOs, shown in Figure 32 and Figure 33, reveal that these crystallise in one of two phases: orthorhombic or rhombohedral. These structures are in line with previously reported studies on thin films of  $La(Cr_{0.2}Mn_{0.2}Fe_{0.2}Co_{0.2}Ni_{0.2})O_3$ .<sup>[167]</sup> Out of the fourteen compositions being studied, four compositions (PS-11, PS-12, PS-13, and PS-14) show a multiphase mixture, while the rest are single-phase oxide systems. PS-11, in particular, shows only extra peaks that can be attributed to  $La_2O_3$ , implying that the stoichiometry of the composition is changing, leading to an excess of lanthanum, while still forming the perovskite phase. The secondary phases in the other compositions (marked with asterisks) may stem from the development of mixed transition metal oxides, which cannot be precisely identified. The shift and broadening of peaks observed for the HEPOs, compared to those of the simple perovskite systems ( $LaCrO_3$  and  $LaCuO_3$ ), provide evidence for the strain induced within the HEPO lattices due to the size differences between the constituent cations.

From the four compositions that formed multiple phases, it can be inferred that the inclusion of Cu and Zn together in the system leads to the formation of secondary phases. The ionic radii mismatch between  $Cu^{2+}$  and  $Zn^{2+}$  cations, compared to other transition metal cations (3+), would lead to differential accommodation of these cations, possibly promoting local clustering and phase segregation. They also have a different preferred crystal structure ( $LaZnO_3 \rightarrow$  hexagonal,  $LaCuO_3 \rightarrow$  rhombohedral), creating further discrepancies in their orientation within the lattice.  $Zn^{2+}$  also lacks affinity for octahedral coordination due to its  $d^{10}$  configuration, resulting in substantial enthalpic penalties when forced into the perovskite structure. The higher annealing temperature and duration can also promote the diffusion of Zn, resulting in the formation of Zn-rich phases.  $Cu^{2+}$  also exhibits pronounced JT distortions in an octahedral environment due to its  $d^9$  configuration, creating extensive lattice strain by elongating or compressing the

$\text{BO}_6$  octahedron.<sup>[168]</sup> The excessive local strain created around Cu and Zn cations decreases the formation energy of cation vacancies, enabling their clustering and diffusion out of the crystal. Furthermore, it has been observed that the segregation of Cu and Zn from a high-entropy lattice is correlated. In the  $(\text{Mg}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{Cu}_{0.2}\text{Zn}_{0.2})\text{O}$  system, when Cu segregates out of the lattice, the entropic stabilisation for Zn reduces, accelerating its segregation as well.<sup>[169]</sup> At higher calcination temperatures, there is a possibility for the selective melting of Cu and the sublimation of Zn. These factors, taken together, may help explain why the combination of Cu and Zn results in the formation of a multi-phase mixture during the synthesis of HEPOs.

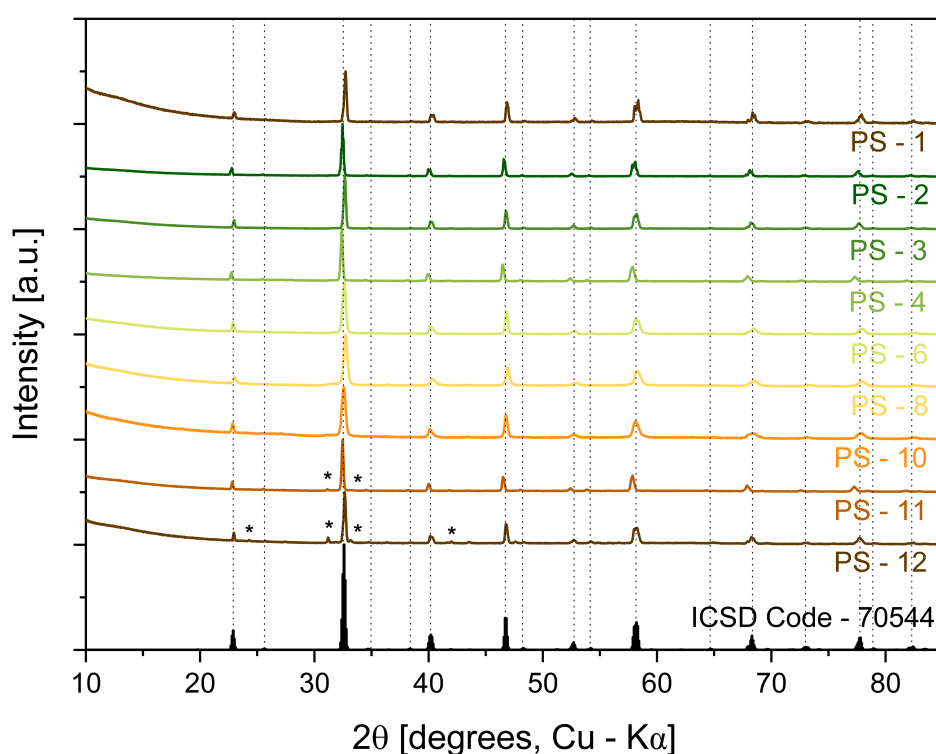


Figure 32: XRD patterns for all samples crystallising in an orthorhombic structure (space group  $Pnma$ ). The asterisks in PS-11 and PS-12 mark the identified peaks originating from secondary phases.

The orthorhombic structures crystallise with the  $Pnma$  space group (ICSD code 70544) as seen in Figure 32, while the rhombohedral structures crystallise with the  $R-3cH$  space group (ICSD code 9428), as seen in Figure 33. HEMs often follow the concept that the structure familiar to most constituents would be imposed on the HEM itself. Comparing the elemental makeup of the two groups reveals correlations between composition and structure, which support the statement. The presence of Cr, Mn, and Fe together in the system compelled it to adopt an orthorhombic structure;  $\text{LaCrO}_3$ ,  $\text{LaMnO}_3$ , and  $\text{LaFeO}_3$  promote the formation of orthorhombic crystals. A similar pattern can also be observed in other compositions containing Co, Ni, and Cu, which are forced into a rhombohedral structure, as evidenced by the rhombohedral phases exhibited by  $\text{LaCoO}_3$ ,  $\text{LaNiO}_3$ , and

LaCuO<sub>3</sub>. For compositions with no clear majority of preferred structure in the parent phases (PS-6, PS-8, PS-10, and PS-12), an orthorhombic structure was still the dominant structure being crystallised. Coincidentally, all these structures contain Zn. This paradoxical behaviour of Zn shifting the material towards an orthorhombic structure has also been noted by Betti et al. in their study of LaBO<sub>3</sub>-type HEOs.<sup>[164]</sup>

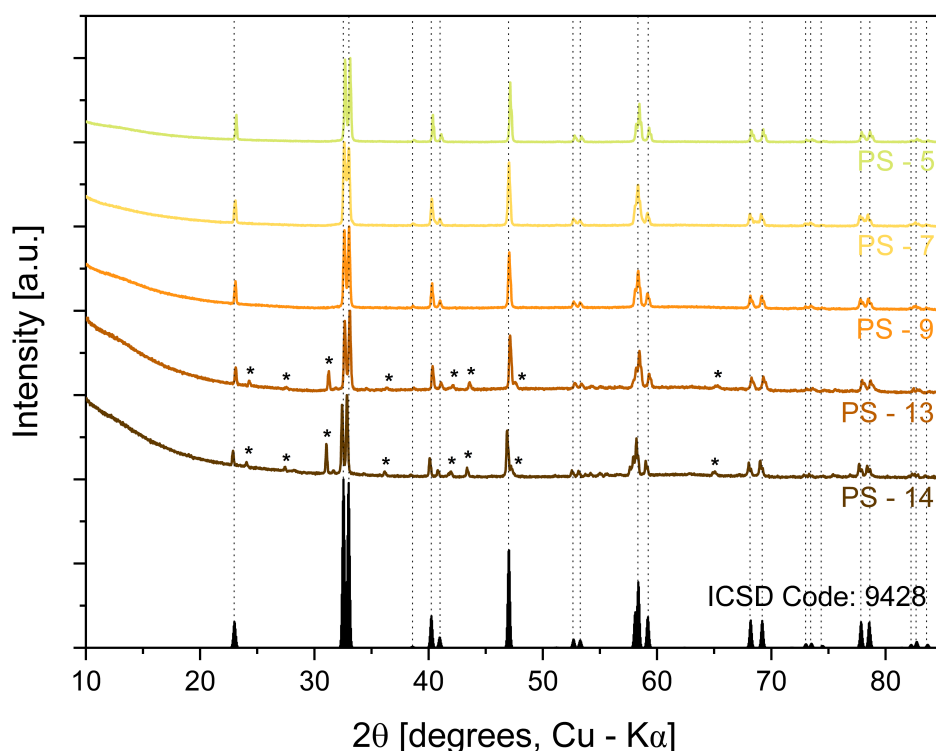


Figure 33: XRD patterns for all samples crystallising in a rhombohedral structure (space group  $R\bar{3}cH$ ). The asterisks in PS-13 and PS-14 mark the identified peaks originating from secondary phases.

The refinement parameters and unit cell dimensions obtained from the Rietveld refinement of the diffraction patterns are presented in Table 9. As expected, the composition without Cu and Zn in the system (PS-8) had the smallest lattice dimensions, as those two are the largest cations within the chosen selection. The general trend also follows the ionic size progression of the transition metals. The size increases as the smaller cations are eliminated from the system. The refinement done on the composition PS-1 is shown in Figure 34(a), and the expected crystal structure is illustrated in Figure 34(b).



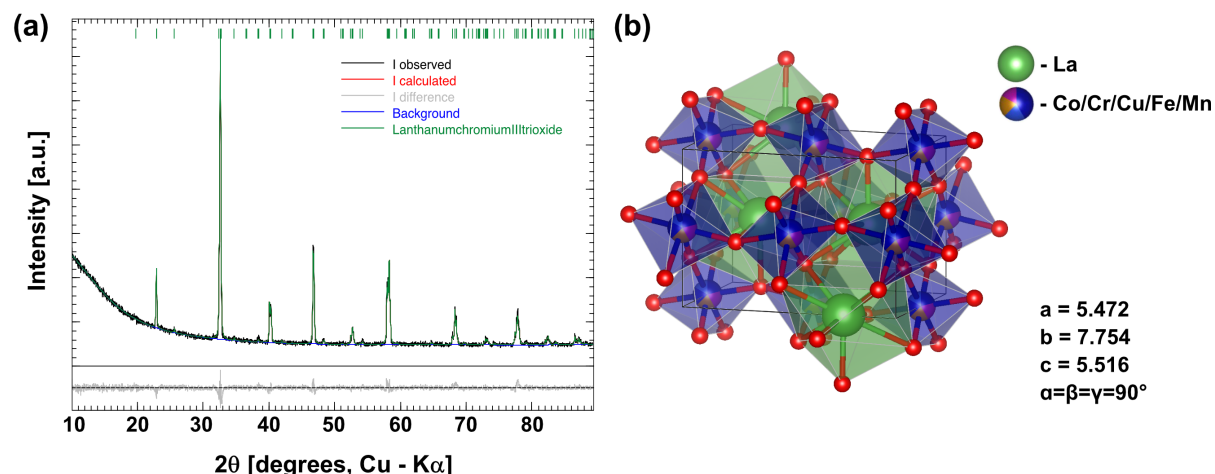


Figure 34: (a) Rietveld refinement based on X-ray diffraction data of PS-1. (b) A visualisation of the crystal structure of the PS-1 modelled on the refinement results. Figure created using Vesta.<sup>[142]</sup>

Table 9: Rietveld refinement parameters for samples exhibiting a single-phase product on calcination. Rietveld refinement done with Profex.

| Sample | $R_{wp}$ | $R_{exp}$ | $\chi^2$ | a (nm) | b (nm) | c (nm) |
|--------|----------|-----------|----------|--------|--------|--------|
| PS-1   | 4.40     | 3.61      | 1.4856   | 0.547  | 0.776  | 0.552  |
| PS-2   | 4.60     | 3.63      | 1.6058   | 0.549  | 0.777  | 0.552  |
| PS-3   | 4.48     | 3.62      | 1.5316   | 0.549  | 0.778  | 0.552  |
| PS-4   | 5.19     | 4.28      | 1.4704   | 0.550  | 0.780  | 0.552  |
| PS-5   | 4.93     | 4.00      | 1.5191   | 0.550  |        | 1.322  |
| PS-6   | 4.23     | 3.56      | 1.4118   | 0.546  | 0.774  | 0.550  |
| PS-7   | 4.75     | 3.94      | 1.4534   | 0.549  |        | 1.319  |
| PS-8   | 4.46     | 3.70      | 1.4530   | 0.543  | 0.780  | 0.550  |
| PS-9   | 4.92     | 3.61      | 1.8574   | 0.550  |        | 1.324  |
| PS-10  | 4.56     | 3.52      | 1.6782   | 0.545  | 0.783  | 0.550  |

### 5.2.1.2 Thin Film Analysis for $\text{LaBO}_3$ -type Perovskites

The thin-film deposition resulted in powdery and porous thin films with inferior adhesion to the substrate. However, the structural analysis of the films showed the formation of the desired perovskite phase, albeit with an impurity of  $\text{La}_2\text{O}_3$  also present in the system. This impurity phase did not disappear even when the stoichiometry of the precursor cation solution was varied, indicating that it arises from a different mechanism. The



spincoating and annealing parameters need to be further optimised to obtain a dense film, which is helpful for optoelectronic applications.

### 5.2.1.3 Powder Analysis for $\text{BiBO}_3$ -, $\text{BaBO}_3$ - and $\text{SrBO}_3$ -type Perovskites

From the other compositions which were also attempted,  $\text{Sr}(\text{CeNbSnYZr})\text{O}_3$  resulted in a perovskite structure (Figure 35(a)). However, on refinement of the structure, it split into two superstructures with slightly varying lattice parameters. The smaller size of the  $\text{Nb}^{5+}$  cation could be a reason for the formation of these superstructures, as it might cause extreme lattice distortion when included with the other larger-sized cations. Variation in the elemental composition may facilitate achieving a homogeneous single-phase HEPO in Sr-based materials. The compositions based on  $\text{BiFeO}_3$  and  $\text{BaTiO}_3$  consistently yielded a multiphase mixture (Figure 35(b) and Figure 35(c)). A possible explanation for this is the difficulty of introducing titanium, vanadium, or niobium into the HEO system, as the precursors required for these elements are not nitrate-based and require additional steps to mix well with the aqueous medium. Moreover, the use of additional chelating agents, such as lactic acid, to promote the mixing of titanium cations in the precursor mix may have led to pockets of elemental segregation, resulting in a multiphase mixture of oxides. The use of solid-state synthesis to address this issue also yielded a similar multiphase mixture of metastable oxides.

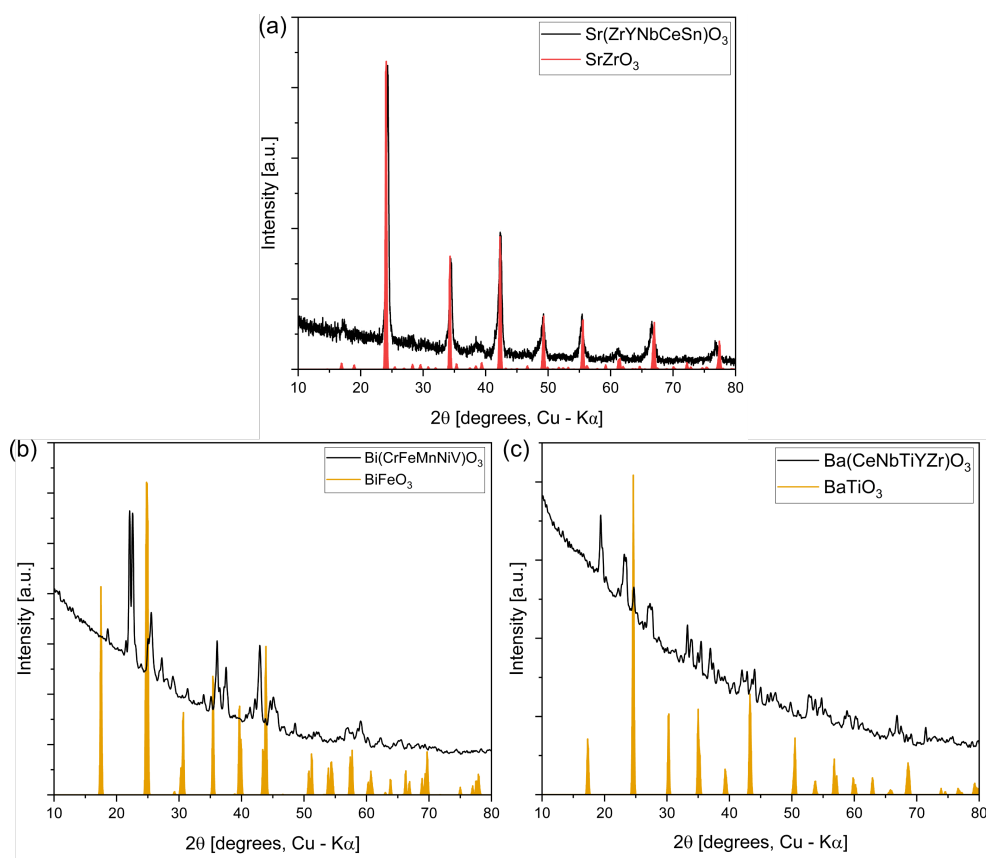


Figure 35: XRD patterns for (a)  $\text{Sr}(\text{ZrYNbCeSn})\text{O}_3$  based on  $\text{SrZrO}_3$ , (b)  $\text{Bi}(\text{CrFeMnNiV})\text{O}_3$  based on  $\text{BiFeO}_3$ , and (c)  $\text{Ba}(\text{CeNbTiYZr})\text{O}_3$  based on  $\text{BaTiO}_3$ .

#### 5.2.1.4 Powder Analysis for $\text{ANbO}_3$ -type Perovskites

Finally, the compositions based on  $\text{KNbO}_3$  also formed a perovskite structure (Figure 36), exhibiting the same issue of superlattice formation, with varying lattice parameters upon further refinement. In this scenario, it is assumed that the smaller size of  $\text{Li}^+$  and  $\text{Na}^+$  ions results in the formation of a different lattice as compared to the larger cations from the other metals present at the A-site. The peak shift from the reference material can be attributed to the extreme lattice distortion present in the system.

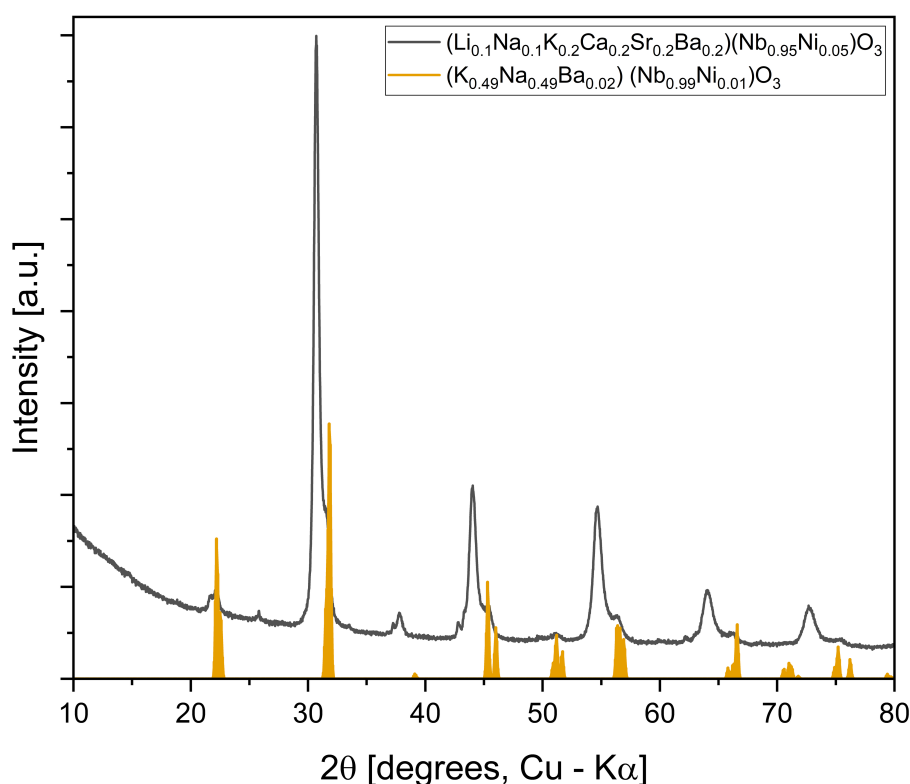


Figure 36: XRD pattern for a HEO based on KNNNO.

### 5.2.2 Morphological and Compositional Analysis

SEM was used to investigate the influence of the elemental composition on the morphological properties of the materials, and EDS was conducted to observe the elemental homogeneity of the system.

For the lanthanum-based HEPOs, it was observed that the crystallite sizes varied significantly, ranging from below 250 nm for PS-10 to over 2.5  $\mu\text{m}$  for PS-1, as shown in Figure 37. A general trend that could be observed was that the addition of Zn resulted in an immediate decrease in the crystallite size, along with forcing the systems to crystallise in an orthorhombic structure. This behaviour can be observed for compositions PS-2, PS-4, PS-6, PS-8, and PS-10, as shown in Figure 39. A possible

explanation for this behaviour can be attributed to the larger size of the  $\text{Zn}^{2+}$ , which causes severe local lattice distortions. These distortions, in turn, can inhibit the crystal growth, leading to smaller crystallites in the final product.<sup>[170]</sup> Control over the surface area of the material can play a crucial role in improving performance for catalytic and electrochemical applications.

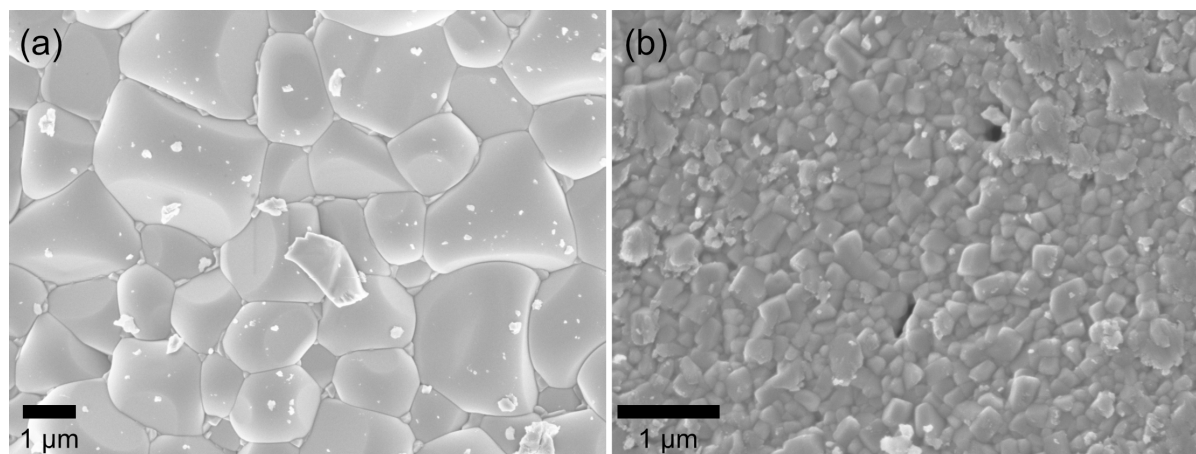


Figure 37: (a) SEM image of a sample without Zn, PS-1 ( $\text{La}(\text{CoCrCuFeMn})\text{O}_3$ ). (b) SEM image of a sample containing Zn, PS-10 ( $\text{La}(\text{CoFeMnNiZn})\text{O}_3$ ).

The EDS mappings for all single-phase compositions indicate a homogeneous distribution of all cations throughout the system on a microscopic scale. Figure 38 shows a representative distribution mapping for sample PS-3. Similar distributions of the B-site cations were observed for the other compositions, too. Table 10 lists the atomic percentages of the compositions as measured by EDS. The composition PS-11 exhibits anomalous behaviour, characterised by islands of La- and Cu-rich phases; however, the secondary phase peaks from X-ray diffraction correspond to only  $\text{La}_2\text{O}_3$ . For most of the compositions, the uniform distribution of the cations along with Rietveld refinement provides evidence for the formation of a single-phase HEPO system without the presence of any large-scale elemental segregation or impurity phases.

The EDS mapping for the prepared thin films revealed the formation of large crystallites of  $\text{La}_2\text{O}_3$ , in addition to the perovskite phase, as shown in Figure 40. There are also small regions of elemental agglomeration, which point to the uneven crystallisation kinetics of the thin-film synthesis. The areas of the film that adhered to the substrate show promise for thin-film electronic applications.

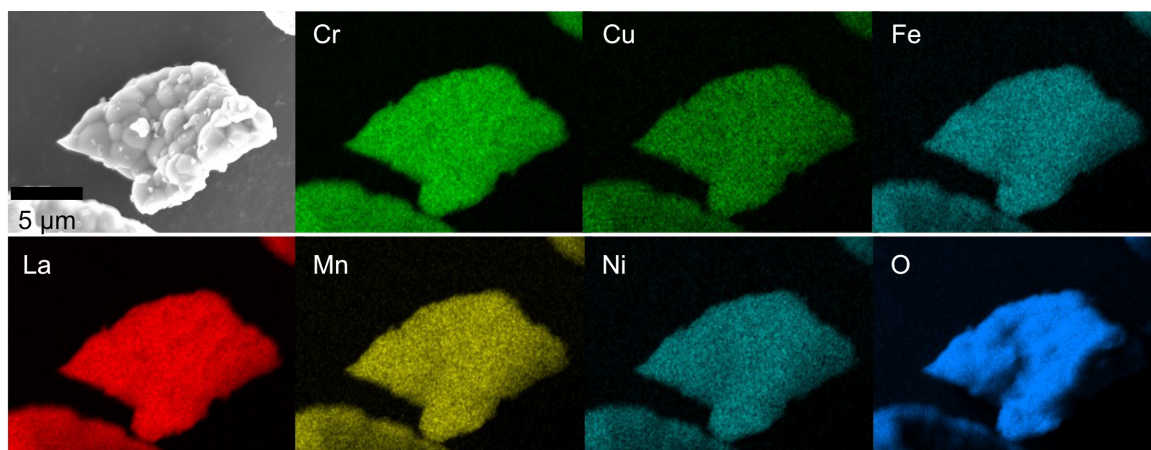


Figure 38: EDS mapping for sample PS-3 ( $\text{La}(\text{CrCuFeMnNi})\text{O}_3$ ).

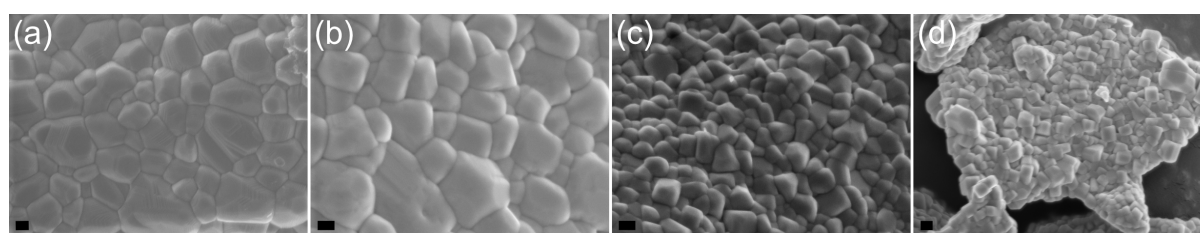


Figure 39: (a) – (d) SEM images of samples containing Zn (PS-2, PS-4, PS-6, PS-8). Scale bar corresponds to a length of 200 nm.

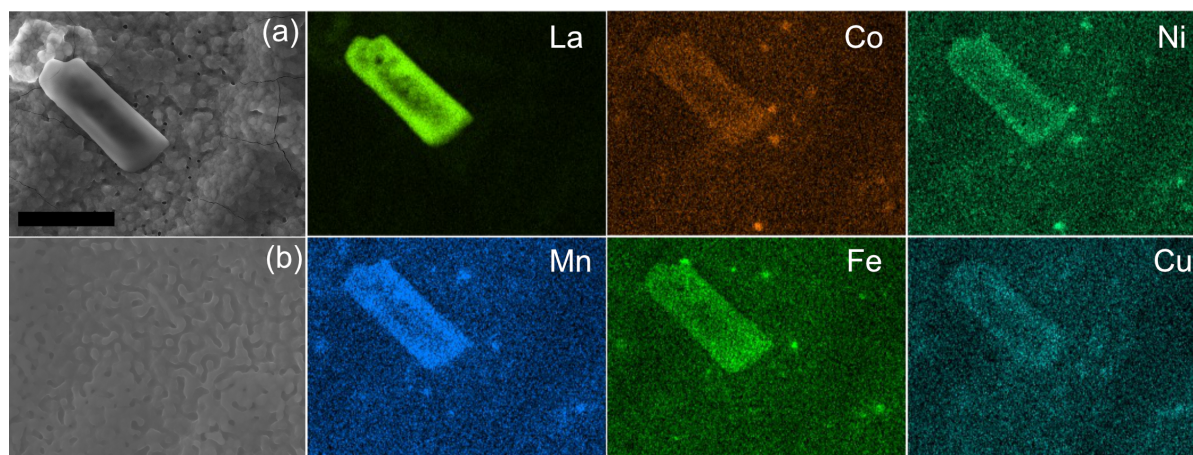


Figure 40: (a) SEM and EDS images for sol-gel deposited thin film of PS-1 showing a crystallite of  $\text{La}_2\text{O}_3$ , and (b) SEM image of a pristine section of the same film. Scale bar corresponds to 10  $\mu\text{m}$ .

Table 10: The elemental percentages for  $\text{LaXO}_3$ -type HEPOs as measured by EDS.

| Sample | Elemental Composition |       |       |       |       |       |       |       |
|--------|-----------------------|-------|-------|-------|-------|-------|-------|-------|
|        | La                    | Cr    | Mn    | Fe    | Co    | Ni    | Cu    | Zn    |
| PS-1   | 51.63                 | 13.15 | 9.25  | 9.2   | 9.38  |       | 7.46  |       |
| PS-2   | 51.91                 | 12.46 | 8.7   | 9.02  | 9.08  |       |       | 8.81  |
| PS-3   | 51.45                 | 12.18 | 8.66  | 8.47  |       | 10.38 | 8.84  |       |
| PS-4   | 52.16                 | 12.65 | 8.92  | 8.78  |       | 10.32 |       | 7.15  |
| PS-5   | 50.55                 | 12.57 | 8.81  |       | 8.79  | 10.13 | 9.16  |       |
| PS-6   | 51.81                 | 12.63 | 8.95  |       | 9.42  | 10.32 |       | 6.88  |
| PS-7   | 52.39                 | 12.36 | 8.4   | 8.82  |       | 10.41 | 7.57  |       |
| PS-8   | 50.37                 | 11.9  |       | 9.01  | 9.59  | 10.47 | 8.61  |       |
| PS-9   | 50.22                 |       | 10.93 | 10.84 | 10.26 | 9.96  | 7.81  |       |
| PS-10  | 52.79                 |       | 9.79  | 9.02  | 9.38  | 10.53 |       | 8.46  |
| PS-11  | 50.68                 | 10.64 | 10.69 | 7.19  |       |       | 10.69 | 10.08 |
| PS-12  | 50.27                 | 10.53 | 11.13 |       |       | 11.65 | 7.1   | 9.3   |
| PS-13  | 48.81                 | 11.83 |       |       | 11.47 | 11.59 | 8.6   | 7.66  |
| PS-14  | 50.73                 |       |       | 11.36 | 11.02 | 11.38 | 9.93  | 5.54  |

### 5.2.3 Raman Spectroscopy

Raman spectroscopy is another technique that helps elucidate the nature of bonds within the structure. For the scope of this work, Raman spectroscopy measurements were performed using a Renishaw confocal optical microscope equipped with a green laser ( $\lambda = 532 \text{ nm}$ ). The measurements were taken over the range of  $10\text{--}1000 \text{ cm}^{-1}$  for 30 seconds, with a total of 10 accumulations.

All the compositions exhibit distinct broad bands at  $510\text{--}540 \text{ cm}^{-1}$  and  $630\text{--}660 \text{ cm}^{-1}$ , along with other lower-intensity peaks. Figure 41 shows the measured Raman spectra for samples PS-1 and PS-9, which exhibit the largest shift. The low-intensity peaks can be attributed to the vibration of the lanthanum sub-lattice, owing to the motion relative to the  $\text{BO}_6$  octahedra. The higher-frequency peak corresponds to the symmetric stretching



vibrations of the  $\text{BO}_6$  octahedra. The lower frequency peak corresponds to the bending and antisymmetric stretching modes of the  $\text{BO}_6$  octahedra. The frequency of these peaks is determined by the extent of JT distortions in the system and can shift with the oxidation state of the cations. The variation in peak frequencies indicates changes in the degree of distortion within the perovskite structure.

Changing the composition at the B-site results in a change in the magnitude of O deflection during vibrations in the O-B-O bond. As the average cation size decreases, the amplitude of bond deflection also decreases, resulting in markedly lower peak intensities. The introduction of lattice strain from cation-size mismatch also causes frequency shifts (usually, smaller cations shift to lower frequencies).

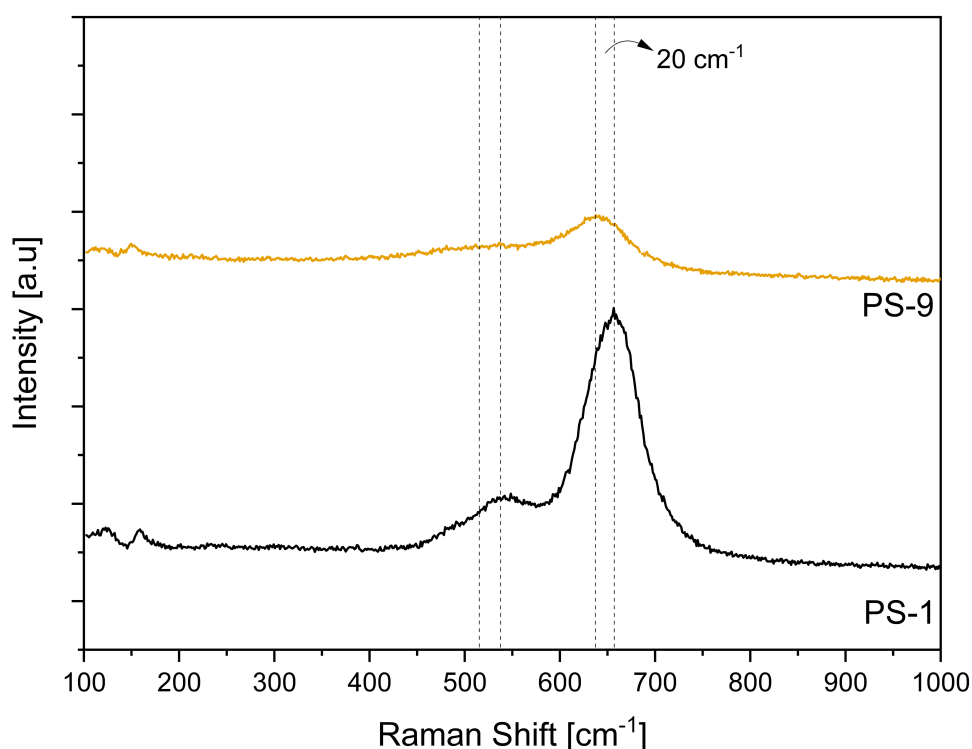


Figure 41: Raman spectra measured on powder samples of PS-1 and PS-9.

#### 5.2.4 Attenuated Total Reflection Infrared Spectroscopy

Attenuated total reflection infrared spectroscopy (ATR-IR) measurements were carried out in the range of 400–4000  $\text{cm}^{-1}$  using an infrared spectrometer equipped with a diamond crystal, which provided the total internal reflection pathway. In the case of metal oxides, the ATR-IR spectra provide information about the B-O bonds present in the system (like Raman spectroscopy). Perovskite oxides generally show peaks below 600  $\text{cm}^{-1}$ , which correspond to the stretching vibrations associated with the B-O bonds.<sup>[171]</sup>

All the compositions exhibit nearly identical ATR-IR spectra within the measured range. A broad peak exists between  $550 - 600 \text{ cm}^{-1}$  (shown in Figure 42), which stems from the B-O bond vibrations within the  $\text{BO}_6$  octahedral, a characteristic peak of perovskites as mentioned earlier. The peak broadening observed here may indicate an increasing magnitude of distortion within the structure. These structural changes may arise from either varying ionic sizes of the cations in the system or from JT distortions, which are often observed in  $\text{LaMnO}_3$  and  $\text{LaCuO}_3$  systems, with a less pronounced effect in other transition-metal perovskite oxides.<sup>[21,172]</sup>

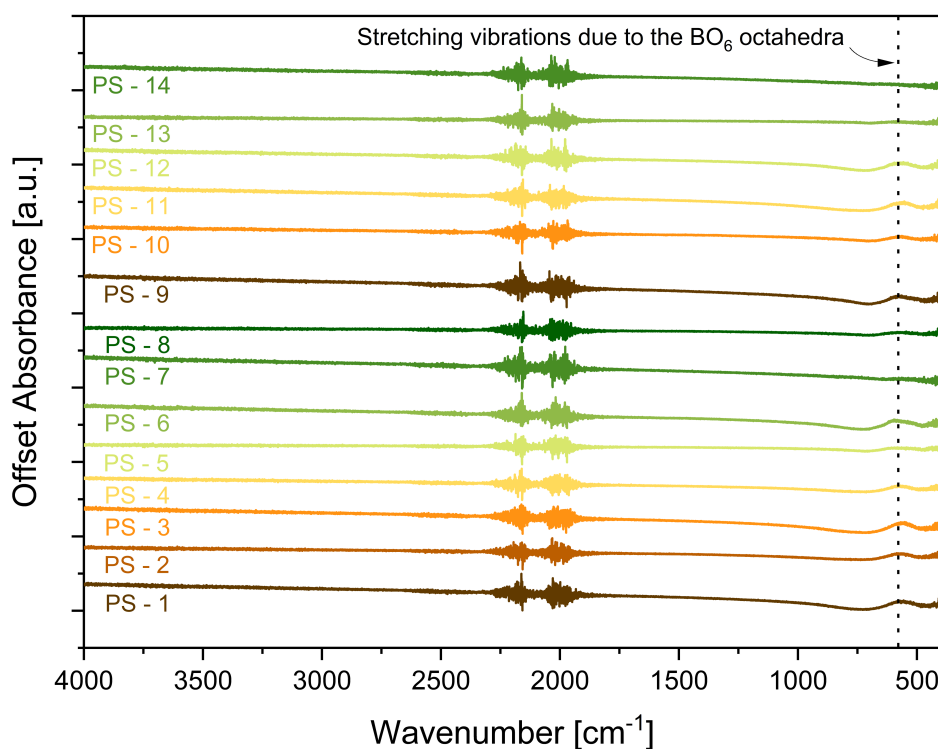


Figure 42: ATR-IR spectra for all prepared samples. The absorption peak between  $550$  and  $600 \text{ cm}^{-1}$  corresponds to the metal-oxygen stretching vibrations from the  $\text{BO}_6$  octahedra present in perovskite oxide structures.

## 5.3 Optical Characterisation

### 5.3.1 UV-Vis Spectroscopy

The absorbance spectra of all the compositions were measured using a Cary 5000 UV-Vis-NIR spectrophotometer equipped with an integrating sphere, operating in reflection mode. The measurements were recorded in the range of  $300 - 1800 \text{ nm}$  using an optically transparent quartz sample carrier with an indentation to hold the powders. Baseline measurements were made on an empty substrate with a 100% reflectance sample as the reference.

All the compositions exhibit a similar absorbance spectrum through these measurements, implying consistent optical characteristics across their breadth. Figure 43 shows the measured spectra for PS-1, with the inset graph illustrating the corresponding Tauc plot. The measured spectra for the remaining compositions are shown in Figure 56 (in the Appendix). As lanthanum-based transition metal perovskite oxides are known to have indirect electronic transitions as the significant source for relaxation of excited electrons, the same has been assumed in the case of these HEPOs; thus, the Tauc plot is plotted with  $n=2$ .<sup>[172]</sup> As shown in the figure, the spectrum is nearly flat over the entire measurement range, without a clear onset, indicating the absence of an optical band edge in this window. The bump and the artefacts observed below 800 nm are due to a sensor change within the device and are independent of the sample being measured. This can also be verified with the Tauc plot, as no intercept can be extracted from it. The most straightforward explanation for this behaviour is that the optical band gap of these HEPOs lies below 0.67 eV (the energy associated with the 1800 nm wavelength).

Another possible explanation for this apparent lack of a band gap is that the HEPOs exhibit metallic behavior and have narrow band gaps. Late transition metals, such as Ni and Cu, have a strong tendency to hybridise their 3d orbitals with the 2p orbitals of O. This overlap of orbitals can result in band broadening within the material, along with the formation of mid-gap states, which both contribute to the contraction of the apparent band gap.<sup>[173–175]</sup> Another attribute often associated with HEPOs is the high density of oxygen vacancies within the system, which arises from the broad spectrum of the formation energies for the oxygen sites, leading to the preferential occupation of these sites by oxygen vacancies, along with the charge imbalances created by the various oxidation states of the constituent cations. These oxygen vacancies, combined with the local structural distortions and high configurational entropy associated with HEPOs, can cause the density of states to extend across the band gap, further obscuring the development of a sharp onset.

Finally, the partially filled d-orbitals of transition metals can lead to strong electron-electron interactions within them. These can further lead to the splitting of the d-orbitals and the associated electronic states for the electrons. This complication in the electronic structure of the system can give rise to Mott-Hubbard (electron-electron repulsion, as seen in  $\text{LaMnO}_3$ ) or charge-transfer insulators (due to the O 2p orbitals lying above the metal d orbitals, as in  $\text{LaNiO}_3$ ). In systems where these interactions dictate the electronic behaviour, conventional band theory breaks down, and electron-electron interactions, rather than band-to-band transitions, govern electronic relaxation.<sup>[176]</sup>



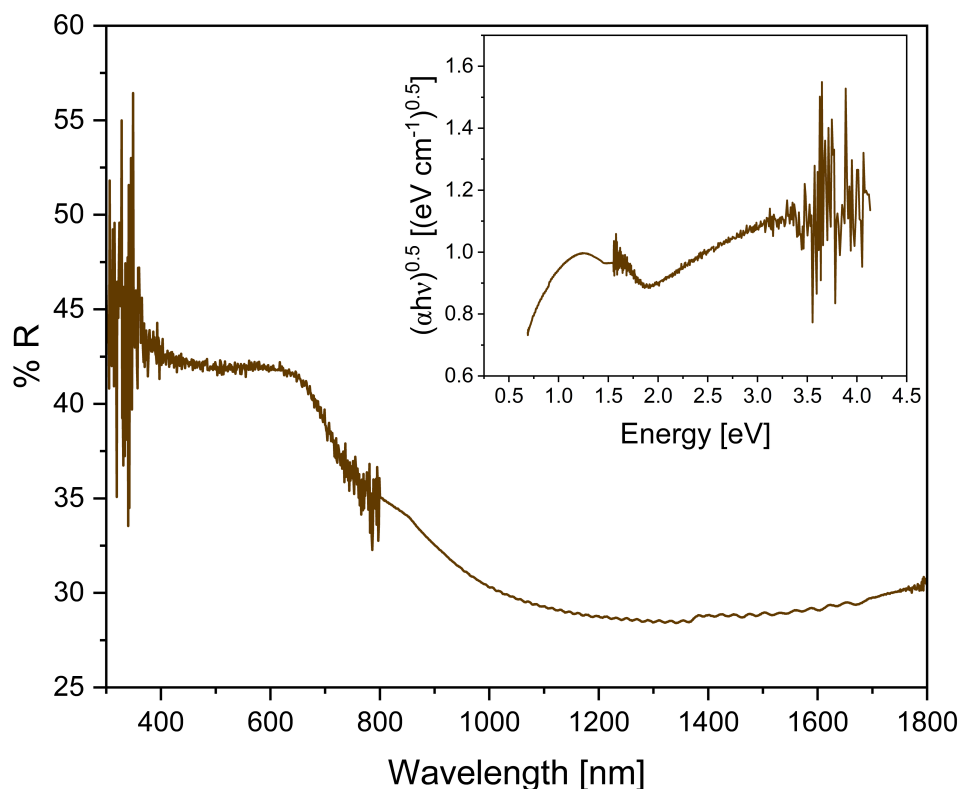


Figure 43: The UV-Vis spectra measured using an integration sphere for sample PS-1 (Tauc plot for indirect transitions inset).

### 5.3.2 Photoelectron Spectroscopy in Air Measurements

To further investigate the band structures of these oxides, PESA measurements were performed to determine the ionisation potentials (IPs) of the prepared materials. The IP provides information about the position of the valence band relative to the vacuum level for these oxides, which is crucial for constructing an optimal solar cell stack and optimising the different layers.

Table 11 shows the variation in the measured IPs across the different samples. There is a noticeable change in the IP from 5.17 eV for PS-9 to 5.72 eV for PS-2, providing evidence for the tuning of IPs via composition changes. A representative measurement from the sample PS-1 is shown in Figure 44. The measurements for the remaining samples are shown in Figure 57 (in the Appendix). Based on the observed values, a general trend emerges: removing Zn from the B-site cationic sublattice decreases the IP, whereas removing Cu increases it. In single-element  $\text{LaBO}_3$  systems, the 3d orbitals shift downward as the transition-metal electronegativity increases, leading to higher IPs, from ~4.8 eV for  $\text{LaMnO}_3$  to ~5.5 eV for  $\text{LaNiO}_3$ .  $\text{LaCrO}_3$ , with an IP of 4.3 eV, is an outlier due to the partially filled d-orbitals.  $\text{Zn}^{2+}$  with its  $d^{10}$  configuration does not take part in the Zn 3d-O 2p hybridisation. It only disturbs the local coordination environment and creates

lattice distortion around it, lowering the valence band minimum (VBM). This may explain the decrease in IP when Zn is removed from the system.<sup>[177]</sup> In the case of  $\text{Cu}^{2+}$ , the single hole from the  $d^9$  configuration can be resonance aligned with the O 2p states, producing maximum hybridisation at the valence band edge, which is not observed in other transition metals.<sup>[178]</sup> This results in a lower IP with the inclusion of Cu as the VBM moves upwards.

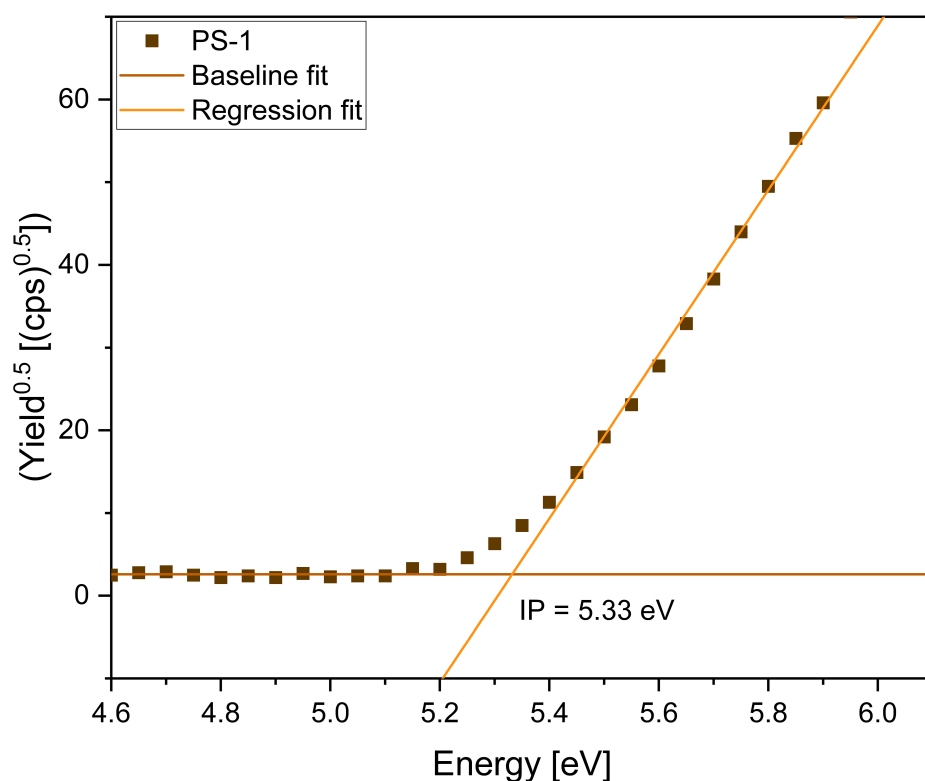


Figure 44: The PESA fit for composition PS-1.

These trends indicate that the electronic structure of HEPOs is highly responsive to the inclusion of specific transition metals, allowing the ionisation potential to be systematically adjusted through deliberate compositional modifications. Such tunability is crucial for optimising energy-level alignment in applications such as solar cells, light-emitting diodes, and photocatalysts, where efficient charge transfer and separation are essential. Moreover, the ability to fine-tune the valence-band edge can impact the material's photostability and interfacial interactions within heterostructures, providing valuable flexibility for designing multifunctional device architectures.

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Table 11: Ionisation potentials for all  $\text{LaXO}_3$ -type compositions.

| Sample | Ionisation Potential (eV) | Sample | Ionisation Potential (eV) |
|--------|---------------------------|--------|---------------------------|
| PS-1   | 5.33                      | PS-8   | 5.37                      |
| PS-2   | 5.72                      | PS-9   | 5.17                      |
| PS-3   | 5.47                      | PS-10  | 5.37                      |
| PS-4   | 5.59                      | PS-11  | 5.39                      |
| PS-5   | 5.48                      | PS-12  | 5.46                      |
| PS-6   | 5.46                      | PS-13  | 5.22                      |
| PS-7   | 5.32                      | PS-14  | 5.17                      |

### 5.3.3 Photoluminescence Spectroscopy

PL spectroscopy is often used to gather information about properties such as band gaps, carrier lifetimes, and defect states of materials, which show potential as absorber layers for perovskite solar cells. For this work, PL and time-resolved PL measurements were carried out by [Pirmin Tischler](#) using a custom-built setup. The powder samples, placed within an indented glass slide, were illuminated with a pulsed Picolo-10 (ND: YVO4 Laser System) from InnoLas, using frequency-tripled light with a wavelength of 355 nm. The pulse frequency was 10 kHz, and each pulse lasted 800 ps. The emitted light from the sample is led through an Acton SpectraPro SP-2300 spectrometer (Princeton Instruments) and recorded by a PI-MAX4 camera (Teledyne Princeton Instruments). All spectra are presented as measured, without correction for system response.

As shown in Figure 45(a), the PL emission spectra for all samples exhibit a similar peak profile when excited by a pulsed laser under vacuum, with significant variance in the measured intensity. Figure 45(b) shows a normalised version of the PL spectra, which helps to compare the peak profiles better. The powder nature of the samples introduces variability in laser absorption due to factors such as packing density, reflectivity, and surface morphology, which can account for the observed discrepancies in emission intensity among the samples. Therefore, normalised intensities are used for comparison. The integrated PL signal exhibits a power-law dependence on excitation intensity with an exponent of  $3.6 \pm 0.9$ , reflecting a strong nonlinear response. The sharp drop-off in the observed intensity for wavelengths exceeding 850 nm can be attributed to the decrease in the detector efficiency for that range. Another peculiar behaviour observed during these measurements was that the emission completely disappeared when conducted under a nitrogen or air atmosphere, with all other characteristics of the setup remaining

unchanged. This implies that there is some environmental sensitivity associated with the photoluminescence emissions, likely arising from quenching or increased thermal dissipative effects associated with the atmosphere used. Oxygen can form reactive singlet species through energy transfer from the excited states, causing heat dissipation, or create charge-transfer complexes that can provide pathways for non-radiative PL recombination. Further work in this direction may open up avenues for utilising these materials in gas sensing and detection applications. Since a power exponent of this magnitude is not typically observed in photoluminescence, a possible explanation is that it stems from thermal emissions instead. This is also further backed by the disappearance of the emissions when measured in an ambient gas atmosphere. Since the measured power exponents of  $3.6 \pm 0.9$  are close to 4, these values align with the theoretical values for blackbody-like thermal radiation as predicted by the Stefan-Boltzmann law.<sup>[179]</sup> To investigate this phenomenon further, the emission spectrum of an incandescent bulb, a known blackbody, was measured using the same experimental setup for comparison. The shape of both spectra shows a strong resemblance, confirming that the PL emissions are due to thermal radiation resulting from laser heating, rather than electronic transitions. Using Planck's radiation law, it can also be estimated that under pulsed excitation, the effective sample temperature can reach values as high as  $2450 \pm 650$  K.

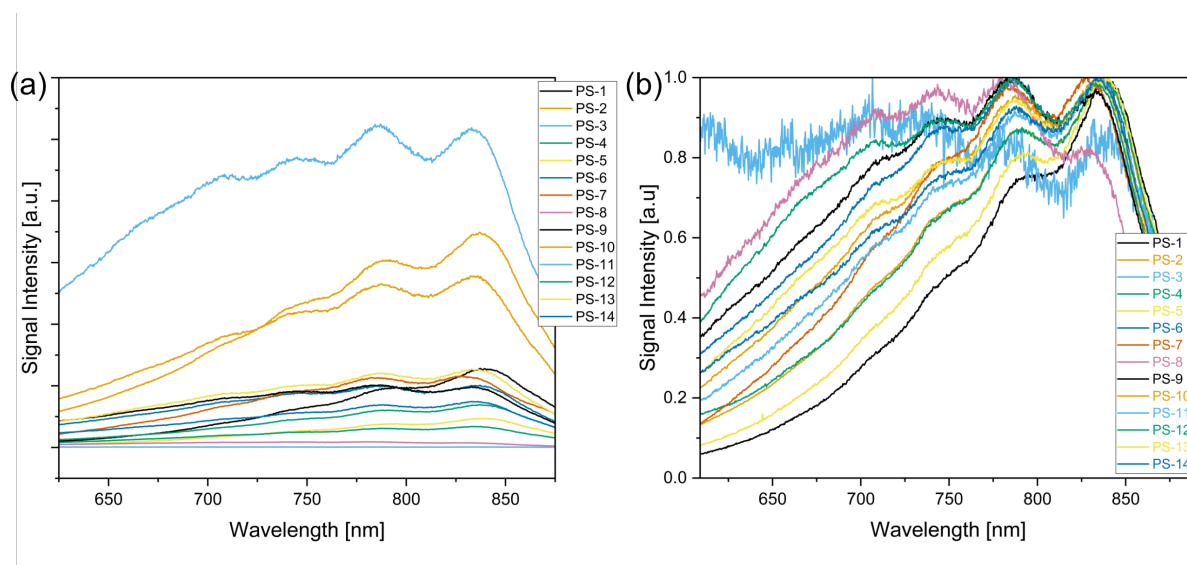


Figure 45: (a) As-measured PL emission for all compositions, and (b) normalised PL emission spectra for all compositions.

Figure 46 shows a representative time-resolved emission spectrum of PS-1; the spectra for the other compositions are not shown here but exhibit similar characteristics. The average lifetime of a thermal emission extracted from these plots is  $48 \pm 38$   $\mu$ s. However, PS-12 exhibits an inconsistent long decay time of 143  $\mu$ s; when this value is excluded from the calculations for the average decay time, the result is reduced to  $38 \pm 24$   $\mu$ s.

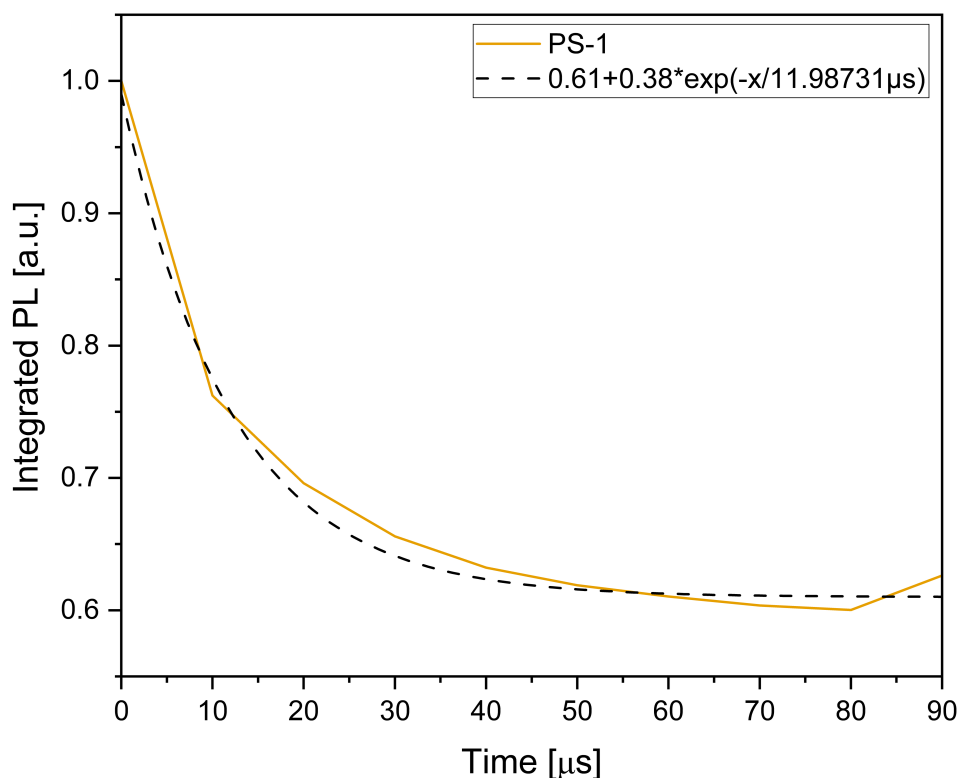


Figure 46: Time-resolved photoluminescence decay for sample PS-1.

## 5.4 Conclusion

To summarise, a series of lanthanum-based HEPOs with diverse transition metal compositions at the B-site, achieving a homogeneous cation distribution, were successfully synthesised. At the same time, more potential compositions based on other perovskite structures, such as  $\text{BaTiO}_3$ ,  $\text{SrZrO}_3$ , and  $\text{KNbO}_3$ , were also investigated; however, these require further fine-tuning before they are ready for applications. In general, the high-entropy strategy serves as a powerful means to modulate both the crystal structure and the electronic band structure of perovskites. Notably, the incorporation of Zn in  $\text{LaBO}_3$ -type systems offers a direct pathway to reducing the particle sizes of the final product. At the same time, simultaneous inclusion of Cu and Zn in such systems leads to the formation of a multiphase mixture owing to the ionic size mismatch between 3+ cations and these two elements. Furthermore, by judiciously selecting parent perovskite templates, the crystal structure can be precisely tailored, allowing flexible control over material properties.

The combined influence of lower 3d orbital energy levels of the transition metals and the lattice distortions inherent to the high-entropy configuration leads to band broadening and broadband absorption. This behaviour indicates the presence of either a narrow

band gap or Mott–Hubbard insulating characteristics, presenting new opportunities for electronic structure engineering. Further DFT studies would be useful in understanding the source of this bandgap narrowing. Additionally, the ionisation potential of these HEPOs can be systematically tuned through compositional design, with Cu and Zn exerting opposite effects on the ionisation energy. Another intriguing observation was the thermal emission resembling black-body radiation detected during photoluminescence measurements under vacuum, revealing efficient photothermal conversion properties.

Overall, this study elucidates the intricate relationships between elemental composition, crystal structure, and optoelectronic behaviour in La-based HEPOs. The demonstrated tunability and unique optical responses position these materials as promising candidates for advanced applications in optoelectronics, infrared sensing, and photothermal technologies. This work, therefore, represents a significant advance toward the rational design of multifunctional perovskite oxides through high-entropy engineering.



## 6 High-Throughput Screening of High-Entropy Fluorite-Type Oxides as Potential Candidates for Photovoltaic Applications

PSCs typically employ an architecture in which the perovskite absorber layer is sandwiched between an ETL and an HTL. Metal oxides are often the preferred choice for these transport layer materials, as they can meet the diverse requirements necessary to achieve high-efficiency PSCs. Ideally, the transport layer materials should exhibit an appropriate band alignment with the perovskite layer to facilitate efficient charge transfer while selectively blocking electrons and holes between the perovskite and the transport layer.

Ceria has been used as an ETL for PSCs, achieving power conversion efficiencies of up to 17% and 23% for doped systems.<sup>[180–182]</sup> CeO<sub>2</sub> possesses intrinsically favourable electronic properties for electron extraction and transport. Cerium readily transitions between Ce<sup>4+</sup> and Ce<sup>3+</sup> oxidation states, forming oxygen vacancies and creating a defect chemistry that can enhance electron transport kinetics.<sup>[183]</sup> This inherent redox flexibility in CeO<sub>2</sub> and its derivatives provides additional pathways for optimising charge dynamics that are not available in systems like TiO<sub>2</sub>, while also helping passivate interfacial defects. It has a wide band gap, which allows for greater optical transparency, and its conduction band exhibits optimal energy level alignment with many existing perovskite materials, thereby enabling the formation of Ohmic contacts at the perovskite-ETL interface through favourable band bending.<sup>[184,185]</sup> These properties help improve carrier extraction efficiencies and minimise energy losses during charge transfer. Tuning the electronic structure of CeO<sub>2</sub> can facilitate the design of more efficient charge transport layers, enabling the development of hybrid systems that enhance the characteristics of perovskite solar cells. Moreover, CeO<sub>2</sub> also enhances device stability as it acts as a diffusion barrier against metal electrode corrosion and moisture ingress. The high density of oxygen vacancies and the Ce<sup>3+</sup> states also help protect the organic components within the device, as they scavenge reactive oxygen species that would normally cause degradation.<sup>[185]</sup> Finally, the low processing temperatures required for ceria make it attractive for large-scale manufacturing and flexible electronics applications.

This study examines the impact of introducing compositional disorder through the incorporation of rare-earth cations in the ceria system on its optoelectronic properties. A high-throughput approach was employed to facilitate the rapid synthesis and screening of rare-earth high-entropy oxides (RE-HEOs) using automated techniques.



## 6.1 Materials Synthesis

### 6.1.1 Powder Preparation

Sixty-four ceria-based compositions containing Ce, La, Pr, Sm, Y, Zr, and Tb were synthesised using a robot-assisted reverse co-precipitation route. These include one composition with all seven elements, seven compositions with six of the seven elements, twenty-one compositions with five of the seven elements, and thirty-five compositions with four of the seven elements. Figure 47(a) and Figure 47(b) provide an overview of the variation in configurational entropy values across the synthesised compositions at 700 °C and 900 °C, respectively. For each cation species, 0.2 M precursor solutions were prepared by dissolving  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich, 99%),  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich, 99.999%),  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (ABCR, 99.9%),  $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich, 99.9%),  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich, 99.8%), and  $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  (Alfa Aesar, 99.9%), and  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (ABCR, 99.9%) in distilled water. These precursor solutions were dispensed into a standard 96-well plate (360  $\mu\text{L}$ ) using an automated pipetting robot (©Opentrons OT-2) in various stoichiometric ratios. A shaker attachment continuously vibrated the well plate to ensure the formation of a homogeneous solution. These prepared mixtures served as a stock solution for further co-precipitation reactions, which take place on various carrier substrates. Different substrates were used depending on the intended characterisation: double-side polished (100) Si wafers for XRD, Macor plates for UV-Vis spectroscopy, and quartz plates for SEM/EDS analysis. Ammonia (Sigma Aldrich, 28%–30%) was used as the base reagent to initiate the coprecipitation reaction. For each sample, 25  $\mu\text{L}$  of the precursor solution was deposited onto the carrier substrate, followed by twice the volume of ammonia (metal: ammonia = 1:2). The deposition process was repeated five times. During the reaction, the carrier substrates were held at 70 °C using a temperature controller to ensure drying of the precipitates. The carrier substrates with the dried precipitates on top were then transferred to a furnace for calcination at either 700 °C or 900 °C for 6 hours with a heating ramp rate of 5 °C  $\text{min}^{-1}$ . The samples were then cooled slowly down to room temperature inside the furnace. The first calcination was conducted in air. To assess the effect of the annealing atmosphere, further calcinations were performed in argon, argon + 10%  $\text{H}_2$ , and again in air, using a flow rate of 60  $\text{L h}^{-1}$  for the gas-controlled atmospheres. After each calcination step, UV-Vis spectra were measured to observe the changes in the band gap energies.

### 6.1.2 Thin-Film Preparation

From the sixty-four compositions, four compositions were selected for further characterisation:  $(\text{La}_{0.25}\text{Tb}_{0.25}\text{Y}_{0.25}\text{Zr}_{0.25})\text{O}_2$ ,  $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Tb}_{0.2}\text{Y}_{0.2}\text{Zr}_{0.2})\text{O}_2$ ,  $(\text{La}_{0.16}\text{Pr}_{0.16}\text{Sm}_{0.16}\text{Tb}_{0.16}\text{Y}_{0.16}\text{Zr}_{0.16})\text{O}_2$ , and  $(\text{Ce}_{0.14}\text{La}_{0.14}\text{Pr}_{0.14}\text{Sm}_{0.14}\text{Tb}_{0.14}\text{Y}_{0.14}\text{Zr}_{0.14})\text{O}_2$ . These are hereafter referred to as REO-4, REO-5, REO-6, and REO-7, respectively. These samples

were chosen because each successive composition introduces one additional element while exhibiting comparable band gap energies, even after annealing under different atmospheres. Larger batches of these compositions were synthesised (~10 g) via reverse co-precipitation to obtain sufficient material to form pellets. The powders were pressed into a 1-inch pellet using a uniaxial press at a pressure of 3 tons. The pellets were then sintered in air at 1200 °C for 12 hours. The sintered pellets served as PLD targets for thin film deposition. Thin films with a thickness of 200 nm were deposited on Si substrates using PLD. The substrates were held at a temperature of 700 °C during the deposition, using a laser fluence of 1.72 J cm<sup>-2</sup> with a frequency of 5 Hz in a chamber with an oxygen partial pressure of 0.05 mbar. The target-substrate distance was set to 2.5 cm, and the laser spot size was 0.04 mm<sup>2</sup>. The aperture for laser input during PLD was kept at 7 mm. After deposition, the substrates were annealed in the PLD chamber at 700 °C and 100 mbar oxygen pressure for 15 minutes to obtain the final RE-HEO films.

## 6.2 Structural and Compositional Characterisation

### 6.2.1 Crystallographic Analysis

The crystal structures of the as-synthesised samples on the Si-substrate were characterised using automated XRD measurements performed on a STOE Stadi P diffractometer, equipped with a Ga-jet X-ray source (Ga-K<sub>β</sub> radiation,  $\lambda = 1.2079 \text{ \AA}$ ) and a custom-built XY stage. XRD patterns were obtained in transmission mode. Patterns were collected between 10° and 60° 2 $\theta$  with a step size of 0.02°. The powder samples on the Si wafer were secured with Kapton foil, and an in-house-designed holder held the wafer in place. A semi-automated Le Bail Fit was done using Topas Academics V5 software for all the samples.

Figure 47(c) and Figure 47(d) show a colour-coded phase map of the obtained oxides. All samples crystallised in one of the following structures: single-phase fluorite-type (space group *Fm-3m*), multi-phase fluorite-type, single-phase bixbyite-type (space group *Ia-3*), or multi-phase mixtures. Table 14 and Table 15 (in the Appendix) present the crystal structure parameters and the chemical compositions of all sixty-four samples calcined at 700 °C and 900 °C, respectively.

# High-Throughput Screening of High-Entropy Fluorite-Type Oxides as Potential Candidates for Photovoltaic Applications

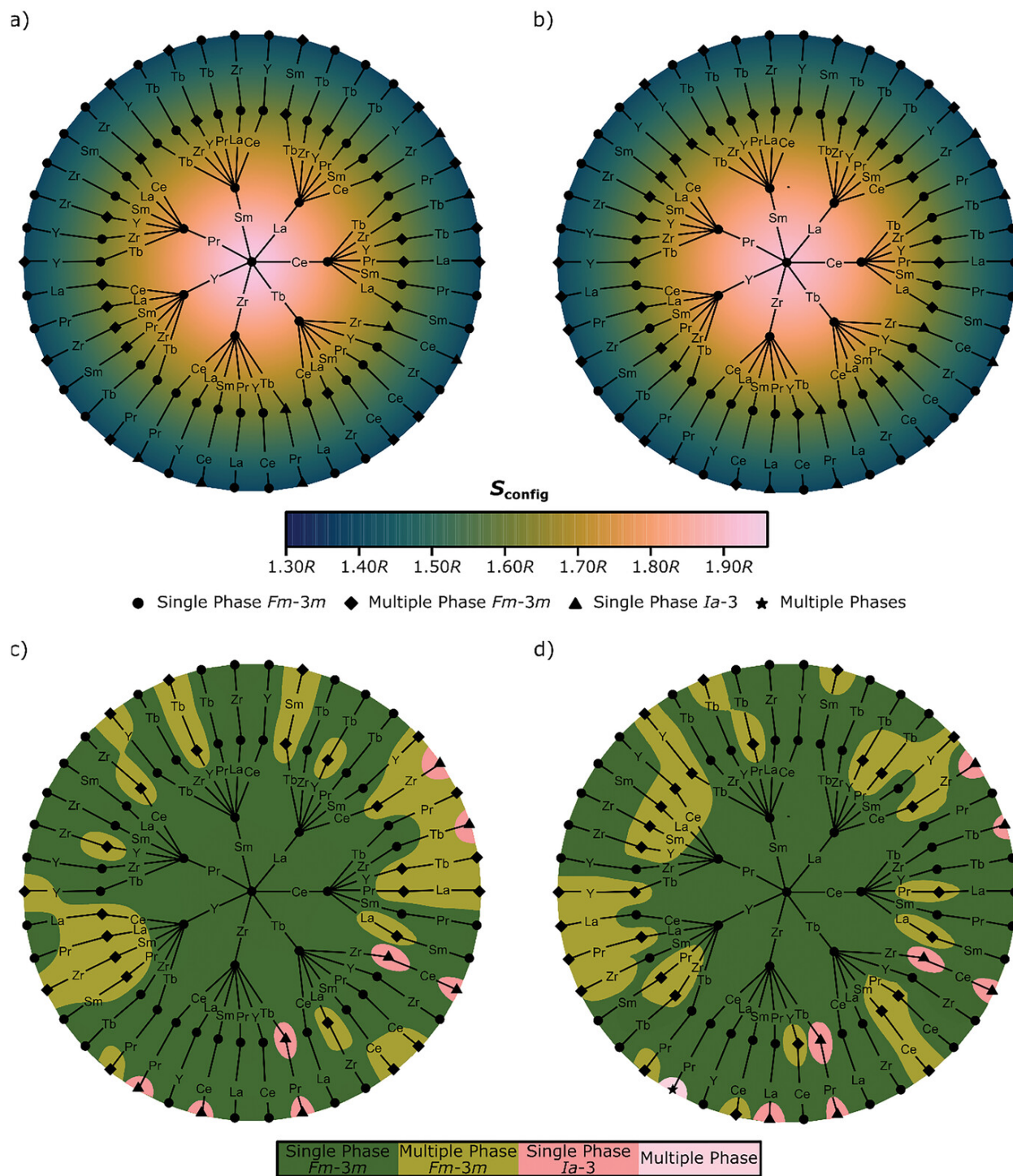


Figure 47: (a) Contour plot of  $S_{\text{config}}$  of the rare-earth oxides calcinated at 700 °C and (b) at 900 °C. Symbols represent the crystal phases. (c) Colour-coded phases of each sample after calcination at 700 °C and (d) 900 °C for better visibility. We note that some compositions are duplicated in this type of chart. "Multiple phase *Fm-3 m*" means that multiple fluorite phases with slightly different lattice parameters were visible in the XRD data. Image from the article by Kumbhakar, Khandelwal et al., published under license CC BY-NC 4.0, 2023.

Based on these results, some general trends can be observed across the compositional space, as summarised in Table 12. Tetravalent cations like  $\text{Ce}^{4+}$  and  $\text{Zr}^{4+}$  play a crucial role in stabilising the *Fm-3m* structure, particularly when other cations are incorporated.

The presence of multivalent cations, such as Tb and Pr, also supports the formation of the fluorite structure, as they can exhibit a 4+ oxidation state. However, due to the smaller ionic radius of the  $Zr^{4+}$  cation, its inclusion often results in the creation of a multi-phase  $Fm-3m$  structure. This effect becomes more pronounced in the absence of multivalent cations, such as Tb. This behaviour can be observed in compositions like  $(Ce_{0.2}Pr_{0.2}Sm_{0.2}YZr_{0.2})O_2$ ,  $(La_{0.2}Sm_{0.2}Tb_{0.2}Y_{0.2}Zr_{0.2})O_2$ , and  $(Ce_{0.25}La_{0.25}Sm_{0.25}Zr_{0.25})O_2$ . In compositions without Ce, while still containing Tb, multiple fluorite phases were obtained, as seen for  $(La_{0.2}Sm_{0.2}Tb_{0.2}Y_{0.2}Zr_{0.2})O_2$  and  $(La_{0.2}Pr_{0.2}Sm_{0.2}Tb_{0.2}Zr_{0.2})O_2$ . The absence of both 4+ cations (Ce and Zr) and multivalent cations (Pr or Tb) favours the formation of the  $Ia-3$  structure. For example, compositions like  $(Ce_{0.25}La_{0.25}Sm_{0.25}Y_{0.25})O_2$ ,  $(La_{0.25}Sm_{0.25}Pr_{0.25}Y_{0.25})O_2$ , and  $(Sm_{0.25}Pr_{0.25}Y_{0.25}Tb_{0.25})O_2$ , which crystallise in the  $Ia-3$  crystal structure independent of the calcination temperature (700 °C and 900 °C). Interestingly, some compositions not containing both Ce and Zr, like  $(La_{0.2}Pr_{0.2}Sm_{0.2}Tb_{0.2}Y_{0.2})O_2$  and  $(La_{0.25}Sm_{0.25}Tb_{0.25}Y_{0.25})O_2$ , still crystallised in the  $Fm-3m$  structure, contradicting the commonly held assumption that Ce or Zr are necessary for the fluorite structure formation.<sup>[16,50,51,111,186]</sup> Previous studies on high-entropy oxides suggest that higher annealing temperatures tend to promote the formation of a single phase. However, in the present study, more single-phase fluorite structures were formed at 700 °C as compared to 900 °C. A few compositions also show a phase change when the annealing temperature is increased from 700 °C to 900 °C. For example,  $(La_{0.25}Sm_{0.25}Y_{0.25}Tb_{0.25})O_2$  changes from a bixbyite phase to a multiphase mixture,  $(La_{0.25}Pr_{0.25}Y_{0.25}Tb_{0.25})O_2$  changes from a bixbyite phase to a superstructure containing two fluorite phases with slightly different lattice parameters, and  $(Ce_{0.25}Sm_{0.25}Y_{0.25}Tb_{0.25})O_2$  changes from a fluorite phase to a bixbyite phase.

Table 12: Summary of observations from the crystallographic analysis of the synthesised HE-REOs. Cations with the prefix "-" are removed, and cations without a prefix are contained in the crystal structure.

| Cation combination | Effect                                   |
|--------------------|------------------------------------------|
| -Zr                | More likely to form single-phase $Fm-3m$ |
| Zr, -Tb            | $Fm-3m$ , multiple phases                |
| -Ce, -Zr, -Tb/Pr   | $Ia-3$ phase                             |
| Tb, -Ce            | Multiple phases                          |
| Ce, Y, Tb/Pr       | Single-phase $Fm-3m$                     |
| >5 cations         | Single-phase $Fm-3m$                     |

Compositions containing Zr also exhibited smaller interplanar spacings compared to other systems, which can be attributed to the smaller ionic radius of  $Zr^{4+}$  relative to the

rare-earth cations used here. Vegard's law states that the lattice parameter of a solid solution is approximately the weighted average of the constituent phases' lattice parameters.<sup>[187]</sup> This leads to a decreasing trend in the lattice parameter with the addition of Zr.

Furthermore, when the synthesis was scaled up to produce a larger batch of powder for pellet pressing, a longer calcination time (12 h) was required for the five- and six-cation RE-HEOs, whereas the four- and seven-cation RE-HEOs formed a single-phase fluorite structure under the same conditions as the high-throughput synthesis (6 h). Figure 48 shows a comparison of the diffraction patterns of the compositions after scale-up.

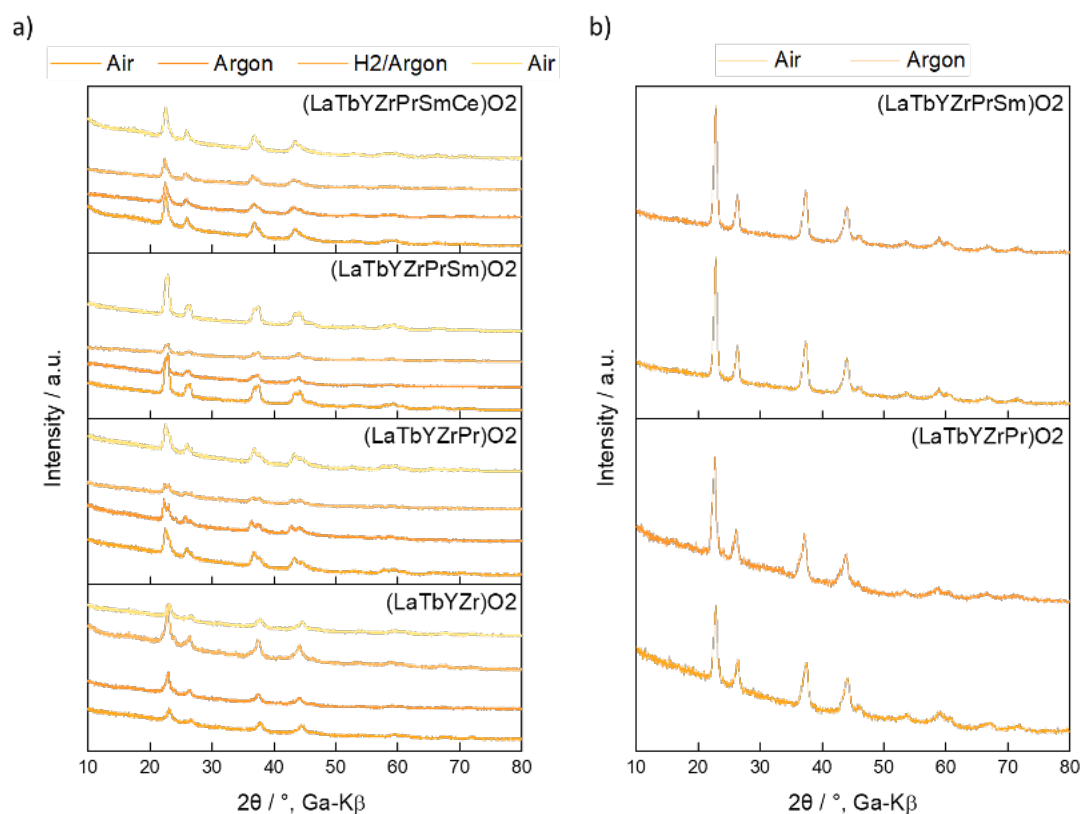


Figure 48: a) XRD-patterns of the fluorite-type oxides calcined at 900 °C for 6 h and different atmospheres. b) Five- and six-component fluorite-type oxide at 900 °C for 12 h at different atmospheres. Image from the article by Kumbhakar, Khandelwal et al., published under license CC BY-NC 4.0, 2023.

Finally, all seven- and six-cation compositions with configurational entropy  $S_{config} > 1.7R$  form a single  $Fm\bar{3}m$  phase at both calcination temperatures. When  $S_{config}$  is reduced by removing constituents to yield five- or four-cation systems, secondary phases and/or temperature-dependent phase transformations emerge. This observation is consistent with the high-entropy stabilisation hypothesis: a large configurational entropy (i.e., a favourable  $-T\Delta S_{config}$  contribution) compensates for the enthalpy of mixing and suppresses phase separation, such that increased cation diversity stabilises the  $Fm\bar{3}m$  structure.<sup>[15,188]</sup> For compositions with  $S_{config} < 1.7R$ , the current data do not allow for a general conclusion regarding phase stability.



## 6.2.2 Compositional Analysis

SEM combined with EDS was performed on samples deposited on a quartz substrate to determine their elemental composition and to assess potential cross-contamination between individual wells. Within the detection limits of EDS, the measured compositions matched the intended stoichiometries, and no cross-well contamination was observed. (Figure 49).

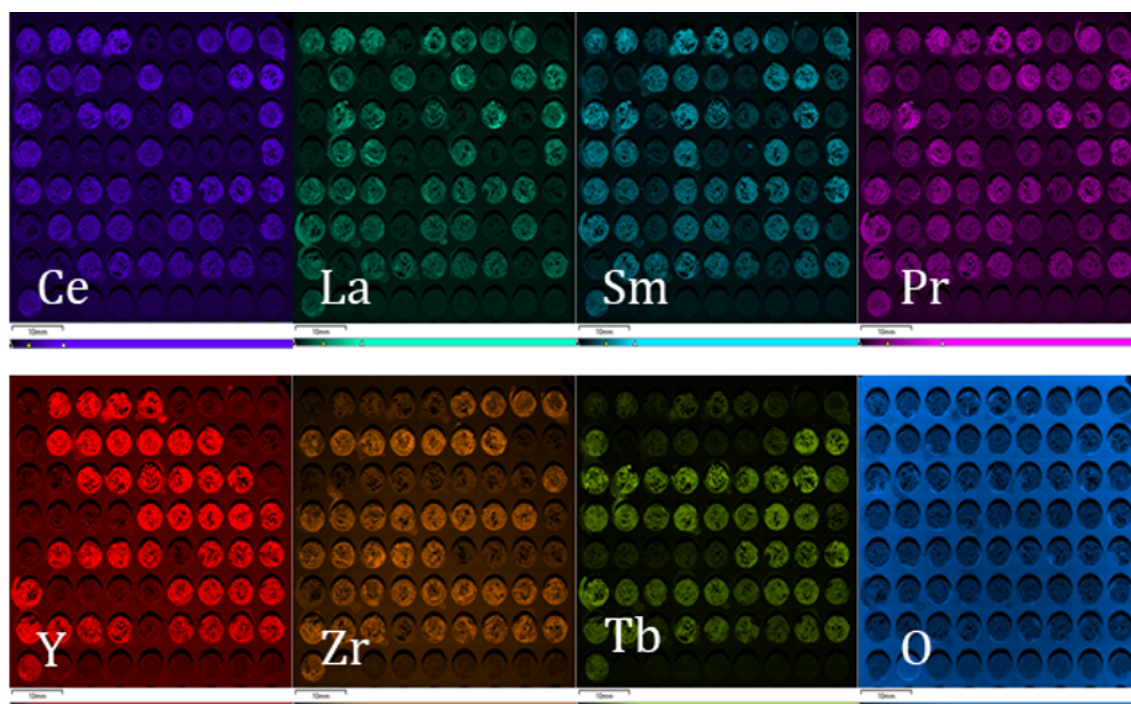


Figure 49: EDS images of samples calcined at 900 °C.

## 6.3 Optical characterisation

Band alignments between different layers in photovoltaic devices are fundamental to achieving high energy conversion efficiency and optimal device performance. The alignment of conduction and valence bands at the heterojunction interfaces directly determines how effectively photogenerated charge carriers can be separated, transported, and collected, making it one of the most critical design considerations in solar cell engineering. Consequently, understanding the band structure of the prepared materials is a crucial prerequisite for assessing their suitability in photovoltaic device architectures.

Diffuse-reflectance UV-vis spectra were collected on a Cary 60 spectrophotometer (Agilent) equipped with a remote fibre-optic diffuse-reflectance accessory (Barreliano). Spectra were recorded from 1100 to 200 nm at a scan rate of 600 nm min<sup>-1</sup> using a custom-built XYZ robot for automated sample exchange. The illuminated spot diameter was approximately 1 mm. Baseline correction was performed using a 100% reflectance reference acquired with an empty Macor substrate. For each sample deposited on a

Macor substrate, five replicate measurements were recorded in reflection mode. A Python script developed by [Mukesh Kumbhakar](#) was used to evaluate the data from the 320 automatically acquired measurements. The automated data acquisition and evaluation were essential to enable the efficient development of the materials libraries.

To further elucidate the band structure, PESA was performed to determine the IPs of a selected set of compositions. In combination with UV-Vis spectroscopy, PESA provides a comprehensive overview of the valence and conduction band energies of the investigated samples. Monochromatic UV photons with an intensity of 1500 nW were used for excitation in the PESA measurements. The photon energy was increased stepwise by 0.05 eV within the range of 5.2–6.2 eV, using an integration time of 10 s per step. Thin-film samples of the selected compositions were deposited by pulse laser deposition prior to the measurements.

### 6.3.1 Dependence on Calcination Temperature

The contour plots shown in Figure 50(a) and Figure 50(b) illustrate the measured optical band gaps of all compositions calcined at 700 °C and 900 °C, respectively. A tabulated comparison of the corresponding values is provided in Table 16 (in the Appendix).

As expected, the compositions calcined at 900 °C generally exhibit a slightly smaller band gap than their counterparts obtained at 700 °C. This decrease can typically be attributed to the enhanced crystallinity and increased particle size of the final product, resulting from a higher synthesis temperature. However, some anomalies can be observed; for instance,  $(\text{Ce}_{0.25}\text{Sm}_{0.25}\text{Pr}_{0.25}\text{Y}_{0.25})\text{O}_2$  exhibits a substantial increase in band gap energy upon calcination at 900 °C. Based on the contour plots, compositions like  $(\text{Ce}_{0.25}\text{La}_{0.25}\text{Sm}_{0.25}\text{Y}_{0.25})\text{O}_2$ ,  $(\text{Ce}_{0.25}\text{La}_{0.25}\text{Sm}_{0.25}\text{Zr}_{0.25})\text{O}_2$ ,  $(\text{Ce}_{0.25}\text{La}_{0.25}\text{Y}_{0.25}\text{Zr}_{0.25})\text{O}_2$ ,  $(\text{Ce}_{0.25}\text{Sm}_{0.25}\text{Y}_{0.25}\text{Zr}_{0.25})\text{O}_2$ ,  $(\text{La}_{0.25}\text{Sm}_{0.25}\text{Y}_{0.25}\text{Zr}_{0.25})\text{O}_2$ , and  $(\text{Ce}_{0.2}\text{La}_{0.2}\text{Sm}_{0.2}\text{Y}_{0.2}\text{Zr}_{0.2})\text{O}_2$  exhibit relatively wide band gaps (3.0–4.9 eV). Notably, all of these samples with wider band gaps lack multivalent cations, such as Tb and Pr. Incorporation of one or both of these multivalent elements results in a significant decrease in the material's band gap. This trend aligns with the previous studies on high-entropy rare-earth oxides and other doped oxide systems, which have reported similar behaviour when multivalent cations are present.<sup>[16,21,51,189–191]</sup> Two primary mechanisms could explain the observed variations in the band gap energies: i) changes in the oxidation state of the constituent elements, resulting in a change in the electronic structure, or ii) the formation of point defects like oxygen vacancies.<sup>[192–198]</sup> Since oxygen vacancies typically induce only minor band gap narrowing effects in the range of approximately 0.3 eV, they are unlikely to account for the pronounced changes observed here. Instead, the considerable reduction in the band gap energies can be attributed to occupation of the RE 4f energy levels introduced by Pr and/or Tb.

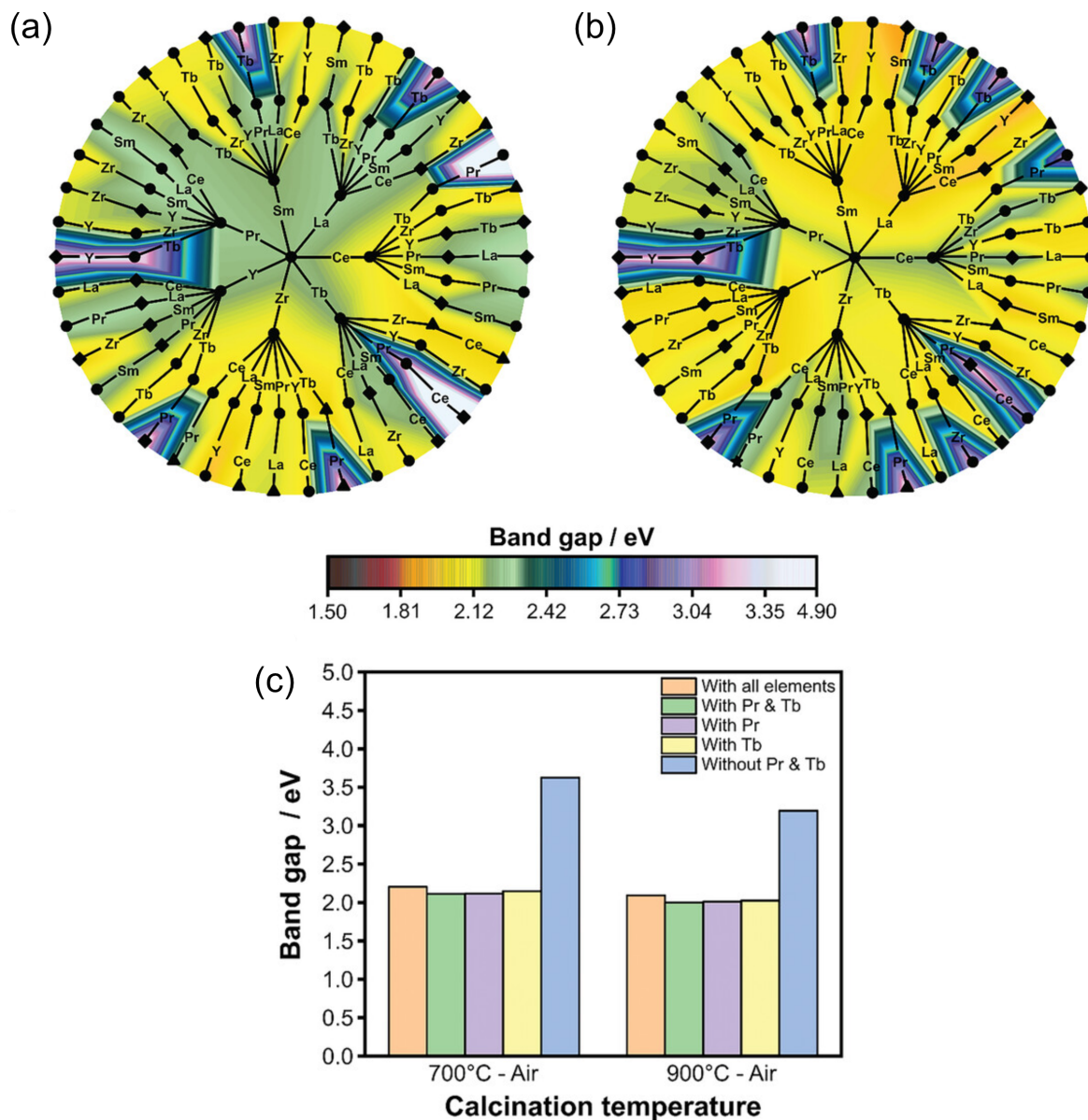


Figure 50: Contour plots of the band gap energies of the REOs calcinated at (a) 700 °C and (b) 900 °C in air. (c) Influence of the cations on the band gap energy. The symbols in (a) and (b) are the same as in Figure 1; the bullet point stands for single-phase  $Fm\bar{3}m$ , the square for multiple  $Fm\bar{3}m$  phases, the triangle for  $Ia\bar{3}$  phases, and the star for multiple different phases. Image from the article by Kumbhakar, Khandelwal et al., published under license CC BY-NC 4.0, 2023.

In rare-earth oxides, the band gap typically arises from the electronic transitions between the RE 5d levels and the O 2p level when the RE 4f level is unoccupied. This is observed in systems like  $\text{CeO}_2$ , which has a band gap of 3.2 eV under standard conditions, as the 4f band is unoccupied. However, when Pr and/or Tb are substituted into the system, they introduce an additional 4f band between the RE 5d and O 2p levels. These intermediate 4f states effectively narrow the band gap to approximately 2 eV.<sup>[50]</sup> This strong dependence of the band gap on the presence of Pr and Tb is consistently observed across all compositions investigated in this study (Figure 50(c)).



### 6.3.2 Dependence on Calcination Atmosphere

As mentioned in the previous section, the oxidation states of the constituent cations can significantly influence the band gap energies of oxides. Besides the calcination temperature, the calcination atmosphere is a powerful parameter to control these oxidation states, as demonstrated in prior studies on RE-HEOs. Varying the calcination atmosphere can modulate the band gap energies by inducing oxygen defects and altering the electronic states.

In the scope of this work, the same batch of samples was sequentially calcined under the following atmospheres: air  $\rightarrow$  argon  $\rightarrow$  10% H<sub>2</sub> + argon  $\rightarrow$  air, with one set processed at 700 °C and another at 900 °C. After each calcination step, UV-Vis spectra were recorded. Figure 51 illustrates the resulting variations in band gap energies for the different calcination atmospheres and temperatures, while Table 17 and Table 18 (in the Appendix) list the corresponding values. Calcination in reducing atmospheres (with low oxygen content) resulted in an increase in the band gap for most compositions. Subsequent annealing in air reversed this increase, indicating that the changes are not permanent. This reversibility was more pronounced in the 700 °C samples, whereas the 900 °C samples exhibited a broader compositional range, with elevated band gap energy values remaining higher. It is well known that the 3+ oxidation states of La, Sm, and Y remain stable across different calcination temperatures and atmospheres. The 4+ oxidation state of Zr also exhibits similar behaviour. In contrast, the oxidation states of Ce, Pr, and Tb can be reduced from 4+ to the 3+ oxidation state under low-oxygen atmospheres, such as argon and 10% H<sub>2</sub> + argon. In this reduced state, the 4f states of these cations, which are located between the RE 5d and O 2p levels, can be partially occupied. As a result, the electronic transition shifts from O 2p  $\rightarrow$  RE 5d (when 4f is unoccupied) to O 2p  $\rightarrow$  RE 4f (when 4f is occupied). These changes in oxidation states are also accompanied by the formation of oxygen vacancies within the lattice, as reported in previous studies. However, the band gap narrowing typically associated with oxygen vacancies (~0.3 eV) is minor compared to the more substantial band gap widening induced by electronic structure changes and thus plays only a negligible role in this context.

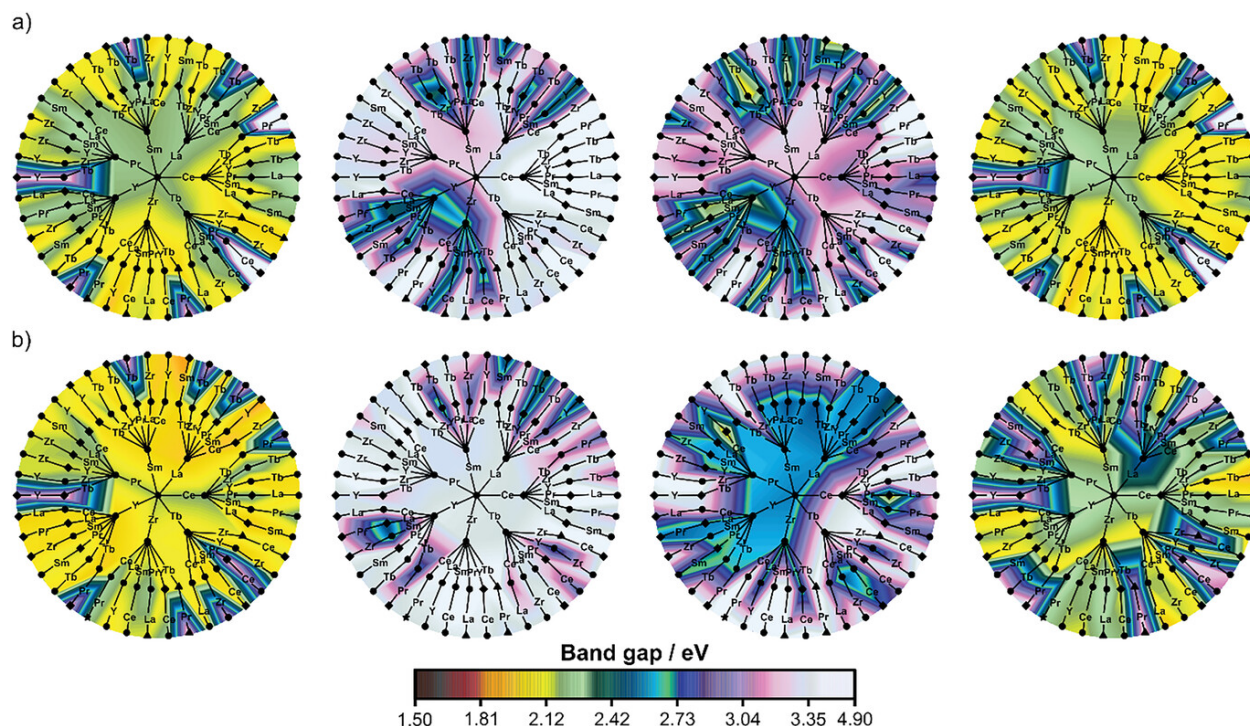


Figure 51: Contour plots of the band gap energies of the RE-HEOs at a) 700 °C and b) 900 °C. From left to right, the atmosphere in which the calcination was performed changes from air to argon to 10% H<sub>2</sub> + argon and back to air. Image from the article by Kumbhakar, Khandelwal et al., published under license CC BY-NC 4.0, 2023.

Interestingly, some deviations from this general behaviour were observed. Samples calcined at 900 °C in argon exhibited a stronger band gap increase than those annealed at 700 °C, which could be attributed to more extensive cation reduction at higher temperatures, resulting in a greater occupation of the 4f states. In another unexpected trend, samples calcined in a 10% H<sub>2</sub> + argon atmosphere at both 700 °C and 900 °C exhibit smaller band gaps than samples treated in pure argon, even though 10% H<sub>2</sub> + argon is a more reducing atmosphere. This effect may be related to the interaction of hydrogen with the oxide, which can lead to the formation of complex chemical species, such as H<sup>+</sup>, H<sup>0</sup>, and H<sup>-</sup>, resulting in unusual changes in the electronic states.<sup>[199–201]</sup> Hydrogen can affect the electronic structure of oxides in several ways:

1. Interstitial hydrogen can act as a shallow donor with energy levels just below the conduction band edge of oxides, which also increases the n-type conductivity by creating mobile electrons
2. Amphoteric behaviour allows hydrogen to form different impurities (H<sup>+</sup>, H<sup>0</sup>, and H<sup>-</sup>) depending on the local environment. H<sup>+</sup> can form stable O-H linkages within the oxygen sublattice, and H<sup>-</sup> can form metal-hydrogen bridges, generating filled defect states at the lower band gap edge.

In the case of TiO<sub>2</sub>, an insulator-to-metal transition occurs when it is doped with hydrogen, resulting from the creation of shallow donor states. In the presence of a reducing atmosphere or by increasing the hydrogen pressure, defect states can also be

generated in the valence band edge.<sup>[202]</sup> These can lead to the development of slight bandgap narrowing effects, along with changes in the material's electrical properties. In  $\text{WO}_3$ , hydrogen incorporation leads to the formation of O-H-O bridges (hydrogen at interstitial sites), and W-H bonds (electron donation to W 5d orbitals), producing two intermediate bands at about 3 eV and 1 eV, respectively, below the conduction band edge.<sup>[203]</sup> Due to the complicated local environments of high-entropy oxides, it can be assumed that similar effects might also take place in the HEOs synthesised under hydrogen-containing atmospheres. This hypothesis should be further investigated in future work, including DFT studies and detailed spectroscopic measurements.

There is also a visual change in the colour of synthesised oxides depending on the calcination atmosphere, as shown in Figure 52.

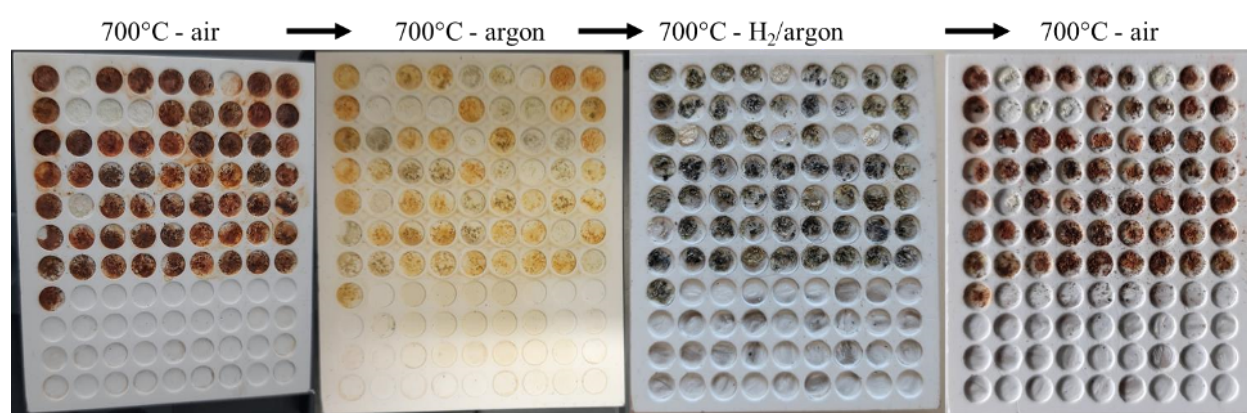


Figure 52: A representation of the optical changes of the prepared REOs with changing calcination atmospheres. Image from the article by Kumbhakar, Khandelwal et al., published under license CC BY-NC 4.0, 2023.

### 6.3.3 Measurement of Ionisation Potentials

PESA was used to measure the IPs of the prepared HEOs. For most oxides, the IP correspond to the edge of the valence band relative to the vacuum level, except in cases where a high density of defect states is present within the band gap. Combining the value of the valence band edge (from PESA) with the optical band gap (from UV-Vis measurements) allows for an estimation of the conduction band edges of these oxides. Once the band structure of the oxide is known, it can be used to precisely match layers in a solar cell stack, ensuring maximum efficiency of charge carrier extraction.

Due to the large number of synthesised samples and the varying synthesis parameters (calcination temperature and atmosphere), it was not feasible to characterise all of them using traditional measurement techniques. Instead, four compositions (REO-4, REO-5, REO-6, and REO-7) were chosen based on the following conditions: (i) they exhibit single-phase structures, (ii) they consistently show small band gaps, and (iii) they represent increasing configurational entropy, i.e., each composition adds one more element to the

previous one. These compositions follow a single compositional path, each differing by exactly one element from the previous one and are summarised in Table 13.

Table 13: Selected compositions with associated band gap energies, crystal structures and configuration entropies.

| Composition                                                                                                                   | Band gap | Crystal structure    | $S_{config}$ | Acronym |
|-------------------------------------------------------------------------------------------------------------------------------|----------|----------------------|--------------|---------|
| $(\text{Ce}_{0.14}\text{La}_{0.14}\text{Pr}_{0.14}\text{Sm}_{0.14}\text{Tb}_{0.14}\text{Y}_{0.14}\text{Zr}_{0.14})\text{O}_2$ | 2.2 eV   | Single phase $Fm-3m$ | 1.95 $R$     | REO-7   |
| $(\text{La}_{0.16}\text{Pr}_{0.16}\text{Sm}_{0.16}\text{Tb}_{0.16}\text{Y}_{0.16}\text{Zr}_{0.16})\text{O}_2$                 | 2.1 eV   | Single phase $Fm-3m$ | 1.79 $R$     | REO-6   |
| $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Tb}_{0.2}\text{Y}_{0.2}\text{Zr}_{0.2})\text{O}_2$                                      | 2.1 eV   | Single phase $Fm-3m$ | 1.61 $R$     | REO-5   |
| $(\text{La}_{0.25}\text{Tb}_{0.25}\text{Y}_{0.25}\text{Zr}_{0.25})\text{O}_2$                                                 | 2.2 eV   | Single phase $Fm-3m$ | 1.39 $R$     | REO-4   |

As shown in Figure 53, PESA measurements indicate an IP of  $5.6 \pm 0.1$  eV for all four samples. No clear correlation can be inferred between the constituent cations and IP from these values, suggesting that the O 2p level is not significantly influenced by the specific cations present in the lattice. Nevertheless, minor adjustments to the band energies may be possible through the addition or removal of specific cations, which can affect the 4f energy level of Ce. This is achieved by increasing the oxygen vacancy density and creating  $\text{Ce}^{3+}$  states, which pull the valence band maximum upwards by creating partially occupied 4f states and thereby reducing the IP.

The difference between the energy level of the valence band from the vacuum level and the bandgap energy would correspond to the energy level of the conduction band. Since both those values are for the chosen compositions, the conduction bands can be estimated to be 3.47 eV, 3.48 eV, 3.46 eV, and 3.45 eV for REO-4, REO-5, REO-6, and REO-7, respectively. Owing to the presence of Tb in all samples, the conduction band edge can be attributed to its 4f level, which lies about 3.7 eV above the valence band. Considering potential lattice distortions due to cation size mismatch and defect states originating from vacancy formation, the estimated conduction band values are reasonably consistent. Overall, the energies of the valence and conduction band edges lie close to the values generally required for charge transport layers in perovskite solar cells. Further tuning of their electronic structure could yield compositions with improved band edge alignments for integration in a solar cell stack.



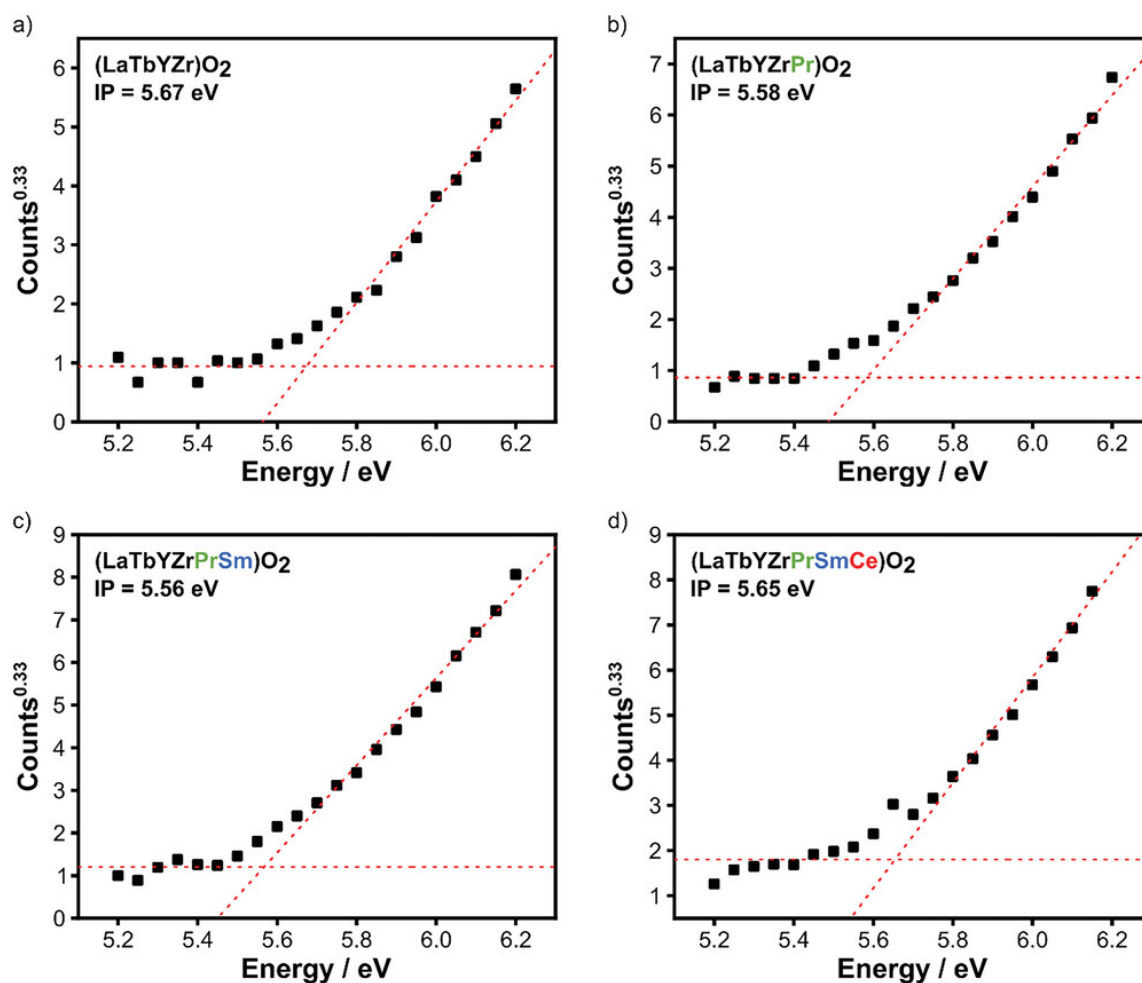


Figure 53: Measurement of the ionisation potential (IP) of the RE-HEOs by PES. Image from the article by Kumbhakar, Khandelwal et al., published under license CC BY-NC 4.0, 2023.

### 6.3.4 Photoluminescence Measurements

For further optical characterisation, PL spectra on thin films of REO-4, REO-5, REO-6, and REO-7 were recorded at an excitation wavelength of 300 nm. Pure  $\text{CeO}_2$  is known to exhibit strong photoluminescence, especially under UV irradiation. This emission originates from charge transfers between  $\text{O}^{2-}$  and  $\text{Ce}^{4+}$  and can be further enhanced by relaxations from the 5d to the 4f level in the presence of  $\text{Ce}^{3+}$ . Additionally, oxygen vacancies can also create additional states for the emission of photoluminescence.

However, as seen from Figure 54, the PL spectra for all four samples exhibit identical peaks that are known artefacts of the device. This distinct absence of any measurable photoluminescence may be attributed to the presence of excess oxygen defects, which act as charge traps and promote non-radiative recombination pathways. Moreover, studies on  $\text{Sm}^{3+}$  doping in  $\text{CeO}_2$  have shown the suppression of photoluminescence due to the elimination of the  $\text{Ce}^{4+}/\text{Ce}^{3+}$  redox couple, thereby preventing the charge-transfer process responsible for photoluminescence generation.

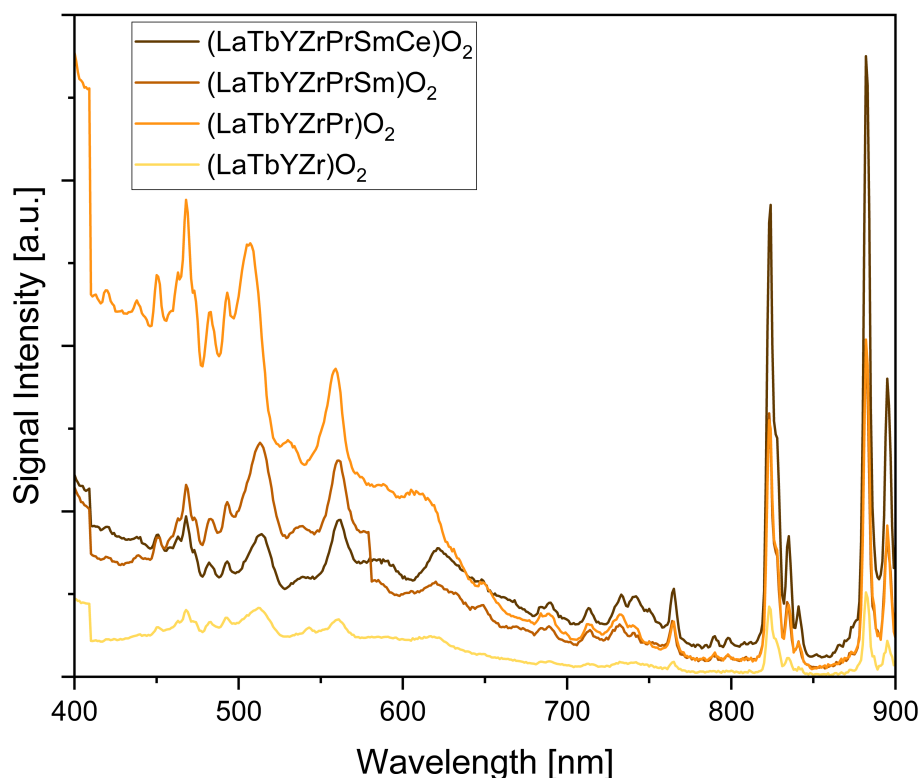


Figure 54: Comparison of the photoluminescence spectrum observed when the REO thin films are irradiated with UV light (300 nm).

## 6.4 Electrical Characterisation

Another important criterion for selecting suitable charge transport layers is their electrical performance, especially charge carrier mobility and electrical conductivity. These properties were measured through Hall-effect measurements conducted on HEO thin-films deposited via PLD. These measurements were performed at room temperature in a magnetic field varying from  $-0.5$  to  $0.5$  T at an applied current of  $0.0009$  mA. The resistivities of the thin films were obtained using the van der Pauw method during the Hall-effect measurements.

As shown in Figure 55, the charge carrier mobilities of the RE-HEO thin films increase with the number of constituent cations, reflecting a direct correlation with the rising configurational entropy. The charge carrier mobilities increase from  $121 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the five-component sample to  $477 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the seven-component system. In ceria and its derivatives, charge transport is primarily electron-based. The predominant n-type conductivity arises from the oxygen vacancies inherently present in them, generating excess electrons localised on the Ce 4f orbitals, which form small polarons. Charge

transport occurs through polaron hopping between neighbouring  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$  ions.<sup>[204]</sup> This n-type conduction is also observed in the RE-HEO films.

Conventionally, increasing the complexity of the system by adding multiple cations would be expected to enhance lattice distortions and defect scattering, thereby reducing charge carrier mobility. However, the RE-HEOs synthesised here show the opposite trend. The composition with the highest configurational entropy shows the maximum charge carrier mobility. In pure  $\text{CeO}_2$ , the charge carrier mobility is generally below  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  because charge transport proceeds via small polaron hopping associated with  $\text{Ce}^{4+}/\text{Ce}^{3+}$  redox couples, which couple strongly to local lattice distortions. Moreover, when  $\text{CeO}_2$  is synthesised under oxidising atmospheres, the concentration of oxygen vacancies and consequently  $\text{Ce}^{3+}$  in the system is negligible, leading to even lower mobilities.<sup>[205]</sup> However, RE-HEOs systems where Pr and/or Tb are incorporated, more sites for small polaron formation are available due to the existence of  $\text{Pr}^{4+}/\text{Pr}^{3+}$  and  $\text{Tb}^{4+}/\text{Tb}^{3+}$  sites. Additionally, due to the high-entropic nature of these compositions, it is possible that Ce also exhibits a higher concentration of  $\text{Ce}^{3+}$  within them. All these effects together expand the available hopping network for polarons, thereby increasing the overall mobility. The observed exceptionally high mobilities compared to pure  $\text{CeO}_2$  may thus result from this enhanced hopping network. Additionally, the lattice strain caused by increased structural disorder could also lower the energy landscape for hopping by modifying the polaron formation energies and preferred migration pathways.<sup>[206]</sup>

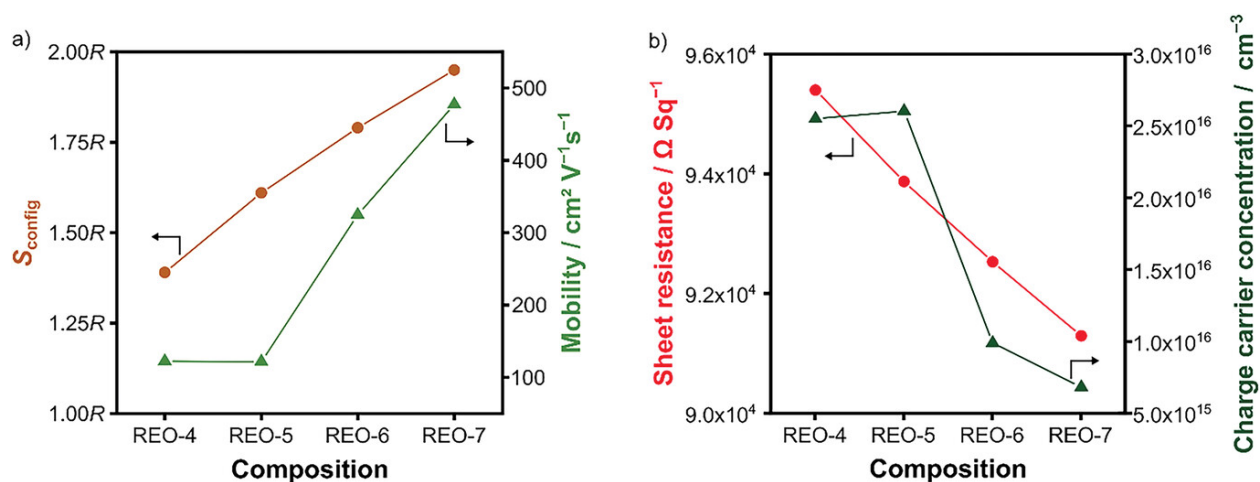


Figure 55: (a) Configurational entropy and electron mobility of the different REO compounds. (b) Sheet resistance and charge carrier concentration. Image from the article by Kumbhakar, Khandelwal et al., published under license CC BY-NC 4.0, 2023.

In contrast to the general trend, the charge carrier concentration (CCC) has decreased with increasing configurational entropy, while the mobilities increase. Usually, a lower CCC would reduce the mobility due to (i) an increase in energetic disorder can lead to a higher density of potential scattering sites, (ii) this can also cause an increase in the recombination of charge carriers, and (iii) lower charge carrier concentration can shift

the transport mechanism to a more thermally activated process. This converse behaviour has previously been reported in ruthenium-doped ceria thin films, which showed a mobility of  $583.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  while still having a CCC lower than pure ceria.<sup>[207]</sup> In the present case, as the mobility increases, it becomes the dominant factor governing the charge transport, leading to a corresponding decrease in sheet resistance. This behaviour indicates that the highest mobility is achieved at lower electron concentrations, suggesting that electron–electron scattering limits charge carrier transport at higher carrier densities.

## 6.5 Conclusions

In this study, sixty-four ceria-based RE-HEO compositions containing Ce, La, Pr, Sm, Y, Zr, and Tb were synthesised and characterised using high-throughput techniques. The majority of these crystallised with a single-phase  $Fm\bar{3}m$  (fluorite) structure, with some outliers forming an  $Ia\bar{3}$  (bixbyite) structure or a multi-phase mixture, depending on the calcination temperature and atmosphere. The presence of Ce together with multivalent cations such as Pr or Tb was found to strongly promote the formation of a single-phase fluorite structure. The various calcination treatments offer a pathway for reversible band gap tuning across a range of compositions, as determined by UV-Vis spectroscopy. Incorporation of Pr and/or Tb resulted in a substantial reduction of the band energies, from 4 eV to 2 eV, mainly due to the incorporation of occupied 4f levels. Additionally, annealing in a reducing hydrogen atmosphere might have resulted in hydrogen incorporation into the lattice, contributing to bandgap narrowing.

Four compositions,  $(\text{La}_{0.25}\text{Tb}_{0.25}\text{Y}_{0.25}\text{Zr}_{0.25})\text{O}_2$ ,  $(\text{La}_{0.2}\text{Pr}_{0.2}\text{Tb}_{0.2}\text{Y}_{0.2}\text{Zr}_{0.2})\text{O}_2$ ,  $(\text{La}_{0.16}\text{Pr}_{0.16}\text{Sm}_{0.16}\text{Tb}_{0.16}\text{Y}_{0.16}\text{Zr}_{0.16})\text{O}_2$ , and  $(\text{Ce}_{0.14}\text{La}_{0.14}\text{Pr}_{0.14}\text{Sm}_{0.14}\text{Tb}_{0.14}\text{Y}_{0.14}\text{Zr}_{0.14})\text{O}_2$ , were selected for further characterisations after scaling up their synthesis, as high-throughput techniques were not possible for these larger sample amounts. PESA measurements revealed that all compositions exhibit very similar ionisation potentials ( $5.6 \pm 0.1 \text{ eV}$ ), indicating that high-entropy lattice distortions do not significantly alter the O 2p energy levels. In contrast to pure  $\text{CeO}_2$ , all four samples show no discernible photoluminescence when excited with UV light. Interestingly, Hall-effect measurements revealed that the charge carrier mobility increases exponentially with configurational entropy, reaching  $477 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for the seven-component system. This exceptionally high mobility is attributed to an enlarged hopping network for polarons, the dominant charge carriers in  $\text{CeO}_2$ -type systems.

Overall, this study demonstrates the use of high-throughput techniques for the rapid screening of RE-HEOs with tailored properties for targeted applications. By further expanding the accessible compositional space, RE-HEOs can be engineered with precisely tuned electronic properties, enabling improved band alignment and charge extraction when integrated as charge transport layers in solar cell architectures.





## 7 Summary and Outlook

### 7.1 Summary

This thesis set out to explore the potential of HEMs as a transformative platform for sustainable, lead-free semiconducting materials, with a particular focus on photovoltaic absorber layers and charge transport materials. By applying the high-entropy concept to halide perovskite derivatives, oxide perovskites, and fluorite-type oxides, this work demonstrates that compositional complexity can be used as an effective design parameter for tailoring optoelectronic, structural, and functional properties, while improving chemical and environmental stability.

The first part of this work demonstrated, for the first time, the use of the high-entropy concept on low-dimensional perovskite-derivative halides based on the  $\text{MA}_3\text{Bi}_2\text{I}_9$  structure. A new class of high-entropy iodides was successfully synthesised and stabilised through multi-cationic substitution at the B-site. Structural characterisation confirmed the retention of the low-dimensional perovskite-derived framework, along with secondary phases, for certain compositions. Meanwhile, optical investigations revealed modified band gaps and tunable electronic states. Although the achieved power conversion efficiencies remain insignificant compared to state-of-the-art lead-based perovskites, this work establishes a fundamental proof of concept that high-entropy design can be used to engineer the electronic landscape of lead-free halides and mitigate some of their intrinsic performance limitations.

Building on this, the second section focused on the development of HEPOs as absorber candidates for all-oxide photovoltaic architectures. The successful synthesis of phase-pure, multicomponent perovskite oxides via solution-processable routes demonstrates the compatibility of high-entropy design with scalable processing techniques. Detailed structural, vibrational, and optical analyses showed that band gaps and ionisation potentials can be systematically tuned by compositional engineering at the B-sites. Photoluminescent emissions reveal that these HEPOs behave as blackbody radiators. These results confirm that HEPOs represent a previously unexplored but highly promising materials class for stable, environmentally benign solar absorbers, even though further reductions in defect density and recombination losses are still required for competitive device integration.

The final third of this thesis addressed the high-throughput synthesis and screening of fluorite-type HEOs, particularly  $\text{CeO}_2$ -based systems, as potential alternatives to conventional electron transport layers. By combining automated robotic synthesis, structural and optical screening, this work establishes an accelerated pipeline for the discovery of multicomponent oxide semiconductors. The investigation revealed that band gaps, ionisation potentials, and electrical transport properties are highly sensitive

to compositional fluctuations and annealing conditions, confirming the vast tunability offered by the high-entropy approach. This also underlines their promise as next-generation charge transport layers through band alignment engineering. The work also underscores the importance of high-throughput techniques for navigating the immense compositional landscape of high-entropy systems and their future optimisation.

While none of the investigated high-entropy systems yet match the efficiencies of state-of-the-art lead-based perovskite solar cells, the work presented here establishes a robust scientific foundation for an entirely new class of sustainable photovoltaic materials, defined by entropy-driven functionality.

## 7.2 Outlook

The results presented in this thesis open several highly promising directions for future research. Beyond photovoltaics, the materials developed in this thesis also show substantial promise for photocatalysis, optoelectronics, thermal photovoltaics, sensing, and electrochemical energy storage, where the interplay between disorder, defect chemistry, and electronic structure can be equally transformative.

For high-entropy halide perovskite derivatives, further work should focus on:

1. *Defect passivation.* Using heterovalent doping and molecular additives to suppress defect densities and trap-assisted recombination.
2. *Dimensional engineering.* Exploring 2D or mixed-dimensional high-entropy structures by using A-site cationic substitutions to further tune the electronic band structure and enhance carrier transport.
3. *Interface optimisation and device architecture refinement.* Engineering better band alignments through the selection of charge transport layers.
4. *Long-term environmental stability studies.* Subjecting prototype cells to thermal cycling and operational stress conditions.

In the case of high-entropy perovskite oxides, future research should prioritise:

1. *Defect chemistry.* Engineering defect densities through oxygen vacancies to minimise non-radiative recombination losses commonly observed in oxide semiconductors.
2. *Strain engineering and thin-film growth.* Tuning band structures and carrier mobilities through structural modifications to the crystal.
3. *Composition selection.* Enhance the electrical conductivity of the semiconductors to enable their integration as true absorber layers.
4. *All oxide solar cell stacks.* Using high-entropy absorbers with high-entropy transport layers to realise completely stable, inorganic solar cells.

For high-entropy fluorite-type oxides, the high-throughput approach demonstrated here can be expanded toward:

1. *Creation of combinatorial libraries.* Deposition techniques like PLD and sputtering can be used to create high-entropy thin films with continuous composition gradients.
2. *Machine learning-assisted optimisation.* Datasets obtained experimentally can be directly used to predict optimal compositions using Bayesian algorithms.
3. *Optimisation of chosen properties.* Optical transparency and electrical conductivity can be simultaneously modified for next-generation transport layers.

From a broader perspective, this work reinforces a paradigm shift in materials design, demonstrating that controlled disorder can facilitate the emergence of new functionalities. Combined with high-throughput techniques and data-driven materials science, compositionally complex semiconductors open new avenues for improved behaviours.



## A Appendix

Table 14: Chemical composition and crystal structure parameters for the sixty-four rare earth fluorite-type structure oxides calcined at 700 °C.

| Composition              | Missing elements | Crystal structure     | a-axis (Å) | V (Å <sup>3</sup> ) | Phase fraction (%) | Chemical concentration |       |       |       |       |    |       |
|--------------------------|------------------|-----------------------|------------|---------------------|--------------------|------------------------|-------|-------|-------|-------|----|-------|
|                          |                  |                       |            |                     |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb | Zr    |
| (CeLaSmPr)O <sub>2</sub> | TbYZr            | <i>Fm</i> -3 <i>m</i> | 5.291 (1)  | 148.1 (1)           | 100                | 26.2                   | 25.1  | 25.8  | 22.9  |       |    |       |
| (CeLaSmY)O <sub>2</sub>  | TbPrZr           | <i>Ia</i> -3          | 10.556 (1) | 1176.3 (5)          | 100                | 22.7                   | 26.23 | 23.89 |       | 27.18 |    |       |
| (CeLaPrY)O <sub>2</sub>  | SmTbZr           | <i>Fm</i> -3 <i>m</i> | 5.264 (1)  | 145.9 (1)           | 100                | 22.88                  | 28.19 |       | 23.2  | 25.73 |    |       |
| (CeSmPrY)O <sub>2</sub>  | LaTbZr           | <i>Fm</i> -3 <i>m</i> | 5.310 (1)  | 149.7 (1)           | 100                | 26.35                  |       | 22.59 | 20.56 | 30.5  |    |       |
| (LaSmPrY)O <sub>2</sub>  | CeTbZr           | <i>Ia</i> -3          | 10.541 (1) | 1171.2 (3)          | 100                |                        | 23.61 | 22.67 | 21.27 | 32.45 |    |       |
| (LaSmPrZr)O <sub>2</sub> | CeTbY            | <i>Fm</i> -3 <i>m</i> | 5.269 (5)  | 146.3 (4)           | 10                 |                        |       |       |       |       |    |       |
|                          |                  | <i>Fm</i> -3 <i>m</i> | 5.131 (16) | 135.1 (3)           | 90                 |                        | 24.82 | 20.97 | 20.92 |       |    | 33.28 |
| (CeLaSmZr)O <sub>2</sub> | PrTbY            | <i>Fm</i> -3 <i>m</i> | 5.270 (3)  | 146.4 (3)           | 33                 |                        |       |       |       |       |    |       |
|                          |                  | <i>Fm</i> -3 <i>m</i> | 2.109 (6)  | 133.4 (4)           | 67                 | 19.58                  | 23.28 | 26.43 |       |       |    | 30.71 |
| (CeLaPrZr)O <sub>2</sub> | SmTbY            | <i>Fm</i> -3 <i>m</i> | 5.203 (3)  | 140.9 (3)           | 49                 |                        |       |       |       |       |    |       |
|                          |                  | <i>Fm</i> -3 <i>m</i> | 5.292 (2)  | 148 (2)             | 51                 | 21.27                  | 26.02 |       | 23.94 |       |    | 28.77 |

## Appendix

| Composition              | Missing elements | Crystal structure | a-axis (Å) | V (Å <sup>3</sup> ) | Phase fraction (%) | Chemical concentration |       |       |       |       |       |       |
|--------------------------|------------------|-------------------|------------|---------------------|--------------------|------------------------|-------|-------|-------|-------|-------|-------|
|                          |                  |                   |            |                     |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb    | Zr    |
| (CeSmPrZr)O <sub>2</sub> | LaTbY            | <i>Fm-3m</i>      | 5.270 (3)  | 146.3 (3)           | 100                | 21.66                  |       | 23.94 | 21.08 |       |       | 33.32 |
| (CePrZrTb)O <sub>2</sub> | LaSmY            | <i>Fm-3m</i>      | 5.266 (2)  | 150.5 (3)           | 52                 | 23.67                  |       |       | 25.81 |       | 28.66 | 21.86 |
|                          |                  | <i>Fm-3m</i>      | 5.159 (3)  | 137.7 (4)           | 48                 |                        |       |       |       |       |       |       |
| (CeLaYZr)O <sub>2</sub>  | SmPrTb           | <i>Fm-3m</i>      | 5.207 (4)  | 145.5 (1)           | 100                | 18.75                  | 22.52 |       |       | 35.29 |       | 23.44 |
| (CeSmYZr)O <sub>2</sub>  | LaPrTb           | <i>Fm-3m</i>      | 5.124 (3)  | 143.7 (3)           | 100                | 22.23                  |       | 26.11 |       | 29.37 |       | 22.28 |
| (LaSmYZr)O <sub>2</sub>  | CePrTb           | <i>Fm-3m</i>      | 5.124 (3)  | 134.7 (2)           | 73                 |                        | 24.66 | 22.89 |       | 25.55 |       | 26.9  |
|                          |                  | <i>Fm-3m</i>      | 5.225 (2)  | 141.7 (2)           | 27                 |                        |       |       |       |       |       |       |
| (CePrYZr)O <sub>2</sub>  | LaSmTb           | <i>Fm-3m</i>      | 5.212 (3)  | 141.6 (2)           | 90                 | 24.52                  |       |       | 24.86 | 24.22 |       | 26.4  |
|                          |                  | <i>Fm-3m</i>      | 5.291 (2)  | 148.1(2)            | 10                 |                        |       |       |       |       |       |       |
| (LaPrYZr)O <sub>2</sub>  | CeSmTb           | <i>Fm-3m</i>      | 5.126 (4)  | 134.5(3)            | 83                 | 26.42                  |       |       | 23.93 | 24.75 |       | 24.9  |
|                          |                  | <i>Fm-3m</i>      | 5.213 (3)  | 142.6(2)            | 17                 |                        |       |       |       |       |       |       |
| (SmPrYZr)O <sub>2</sub>  | CeLaTb           | <i>Fm-3m</i>      | 5.235 (6)  | 143.9(3)            | 100                |                        |       | 24.84 | 23.56 | 25.18 |       | 26.41 |
| (CeLaSmTb)O <sub>2</sub> | PrYZr            | <i>Fm-3m</i>      | 5.259 (1)  | 141.2(2)            | 100                | 23.45                  | 25.33 | 25.65 |       |       | 25.57 |       |



## Appendix

| Composition              | Missing elements | Crystal structure            | a-axis (Å)             | V (Å <sup>3</sup> )  | Phase fraction (%) | Chemical concentration |       |       |       |       |       |       |
|--------------------------|------------------|------------------------------|------------------------|----------------------|--------------------|------------------------|-------|-------|-------|-------|-------|-------|
|                          |                  |                              |                        |                      |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb    | Zr    |
| (CeLaPrTb)O <sub>2</sub> | SmYZr            | <i>Fm-3m</i><br><i>Fm-3m</i> | 5.319 (3)<br>5.164 (3) | 146.0(2)<br>137.3(3) | 10<br>90           | 26.86                  | 24.21 |       | 21.43 |       | 27.5  |       |
| (CeSmPrTb)O <sub>2</sub> | LaYZr            | <i>Fm-3m</i>                 | 5.289 (1)              | 147.9(1)             | 100                | 24.61                  |       | 27.41 | 20.32 |       | 27.67 |       |
| (LaSmPrTb)O <sub>2</sub> | CeYZr            | <i>Fm-3m</i>                 | 5.258 (1)              | 145.4(1)             | 100                |                        | 26.43 | 24.59 | 23.31 |       | 25.67 |       |
| (CeLaYTb)O <sub>2</sub>  | SmPrZr           | <i>Fm-3m</i>                 | 5.218 (1)              | 142.0(1)             | 100                | 19.67                  | 22.98 |       |       | 31.46 | 25.89 |       |
| (CeSmYTb)O <sub>2</sub>  | LaPrZr           | <i>Fm-3m</i>                 | 5.265 (1)              | 145.9(1)             | 100                | 22.51                  |       | 25.91 |       | 28.41 | 23.17 |       |
| (LaSmYTb)O <sub>2</sub>  | CePrZr           | <i>Ia-3</i>                  | 10.437 (1)             | 1136.9(4)            | 100                |                        | 16.7  | 22.88 |       | 31.89 | 28.53 |       |
| (CePrYTb)O <sub>2</sub>  | LaSmZr           | <i>Fm-3m</i>                 | 5.244 (1)              | 144.2(1)             | 100                | 21.8                   |       |       | 21.62 | 31.5  | 25.08 |       |
| (LaPrYTb)O <sub>2</sub>  | CeSmZr           | <i>Ia-3</i>                  | 10.411 (1)             | 1128.4(4)            | 100                |                        | 27.84 |       | 17.61 | 28.37 | 26.18 |       |
| (SmPrYTb)O <sub>2</sub>  | CeLaZr           | <i>Ia-3</i>                  | 10.474 (1)             | 1149.2(4)            | 100                |                        |       | 24.17 | 24.51 | 26.14 | 25.18 |       |
| (CeLaZrTb)O <sub>2</sub> | SmPrY            | <i>Fm-3m</i>                 | 5.201 (2)              | 144.7(1)             | 100                | 21.1                   | 27.87 |       |       |       | 27.99 | 23.04 |
| (CeSmZrTb)O <sub>2</sub> | LaPrY            | <i>Fm-3m</i>                 | 5.239 (2)              | 143.8(2)             | 100                | 20.89                  |       | 27.75 |       |       | 25.6  | 25.85 |
| (LaSmZrTb)O <sub>2</sub> | CePrY            | <i>Fm-3m</i>                 | 5.205 (4)              | 141.0(3)             | 100                |                        | 23.31 | 26.94 |       |       | 27.51 | 22.23 |
| (LaPrZrTb)O <sub>2</sub> | CeSmY            | <i>Fm-3m</i>                 | 5.150 (5)              | 136.6(4)             | 100                |                        | 26.48 |       | 23.56 |       | 25.45 | 24.51 |

## Appendix

| Composition                | Missing elements | Crystal structure     | a-axis (Å) | V (Å³)    | Phase fraction (%) | Chemical concentration |       |       |       |       |       |       |
|----------------------------|------------------|-----------------------|------------|-----------|--------------------|------------------------|-------|-------|-------|-------|-------|-------|
|                            |                  |                       |            |           |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb    | Zr    |
| (SmPrZrTb)O <sub>2</sub>   | CeLaY            | <i>Fm</i> −3 <i>m</i> | 5.229 (3)  | 142.9(2)  | 100                |                        |       | 25.44 | 23.12 |       | 28.77 | 22.67 |
| (CeYZrTb)O <sub>2</sub>    | LaSmPr           | <i>Fm</i> −3 <i>m</i> | 5.195 (2)  | 140.2(2)  | 100                | 16.28                  |       |       |       | 29.54 | 34.5  | 19.67 |
| (LaYZrTb)O <sub>2</sub>    | CeSmPr           | <i>Fm</i> −3 <i>m</i> | 5.157 (4)  | 137.2(3)  | 100                |                        | 23.88 |       |       | 28.83 | 33.09 | 14.2  |
| (SmYZrTb)O <sub>2</sub>    | CeLaPr           | <i>Fm</i> −3 <i>m</i> | 5.204 (3)  | 140.9(3)  | 81                 |                        |       | 29.76 |       | 26.82 | 22.4  | 21.02 |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.040 (7)  | 128.0(5)  | 19                 |                        |       |       |       |       |       |       |
| (PrYZrTb)O <sub>2</sub>    | CeLaSm           | <i>Fm</i> −3 <i>m</i> | 5.175 (5)  | 138.6(4)  | 100                |                        |       |       | 22.68 | 27.37 | 29.35 | 20.61 |
| (CeLaSmPrY)O <sub>2</sub>  | TbZr             | <i>Ia</i> −3          | 10.560 (1) | 1177.5(4) | 100                | 18.64                  | 18.41 | 19.11 | 16.21 | 27.63 |       |       |
| (CeLaSmPrZr)O <sub>2</sub> | TbY              | <i>Fm</i> −3 <i>m</i> | 5.251 (2)  | 144.8(2)  | 100                | 19.66                  | 22.71 | 19.51 | 19.1  |       |       | 19.02 |
| (CeLaSmYZr)O <sub>2</sub>  | PrTb             | <i>Fm</i> −3 <i>m</i> | 5.218 (4)  | 142.1(3)  | 100                | 17.26                  | 16.42 | 19.58 |       | 26.09 |       | 20.66 |
| (CeLaPrYZr)O <sub>2</sub>  | SmTb             | <i>Fm</i> −3 <i>m</i> | 5.230 (8)  | 143.1(6)  | 100                | 16.41                  | 20.32 |       | 16.5  | 22.45 |       | 24.32 |
| (CeSmPrYZr)O <sub>2</sub>  | LaTb             | <i>Fm</i> −3 <i>m</i> | 5.274 (3)  | 146.7(2)  | 83                 | 17.93                  |       | 21.81 | 17.19 | 18.01 |       | 25.05 |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.106 (7)  | 133.1(6)  | 17                 |                        |       |       |       |       |       |       |
| (LaSmPrYZr)O <sub>2</sub>  | CeTb             | <i>Fm</i> −3 <i>m</i> | 5.219 (4)  | 142.1(3)  | 100                |                        | 21.97 | 21.98 | 19.7  | 20.01 |       | 16.34 |
| (CeLaSmPrTb)O <sub>2</sub> | Yzr              | <i>Fm</i> −3 <i>m</i> | 5.268 (1)  | 146.2(1)  | 100                | 21.95                  | 22.08 | 19.57 | 17.8  |       | 18.59 |       |

## Appendix

| Composition    | Missing elements | Crystal structure | a-axis (Å) | V (Å³)   | Phase fraction (%) | Chemical concentration |       |       |       |       |       |       |
|----------------|------------------|-------------------|------------|----------|--------------------|------------------------|-------|-------|-------|-------|-------|-------|
|                |                  |                   |            |          |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb    | Zr    |
| (CeLaSmYTb)O₂  | PrZr             | <i>Fm-3m</i>      | 5.250 (1)  | 144.7(1) | 100                | 19.01                  | 16.97 | 17.53 |       | 26.2  | 20.29 |       |
| (CeLaPrYTb)O₂  | SmZr             | <i>Fm-3m</i>      | 5.236 (1)  | 143.5(1) | 100                | 19.3                   | 16.68 |       | 15.19 | 27.32 | 21.52 |       |
| (CeSmPrYTb)O₂  | LaZr             | <i>Fm-3m</i>      | 5.272 (1)  | 146.5(1) | 100                | 18.4                   |       | 20.05 | 17.93 | 23.47 | 20.16 |       |
| (LaSmPrYTb)O₂  | CeZr             | <i>Fm-3m</i>      | 5.241 (1)  | 144.0(1) | 100                |                        | 18.31 | 21.07 | 18.15 | 21.49 | 20.99 |       |
| (CeLaSmZrTb)O₂ | PrY              | <i>Fm-3m</i>      | 5.228 (3)  | 142.9(2) | 73                 | 19.67                  | 21.88 | 20.61 |       |       | 22.03 | 15.81 |
|                |                  | <i>Fm-3m</i>      | 5.080 (9)  | 131.1(7) | 27                 |                        |       |       |       |       |       |       |
| (CeLaPrZrTb)O₂ | SmY              | <i>Fm-3m</i>      | 5.254 (4)  | 145.1(3) | 72                 | 17.48                  | 17.59 |       | 19.52 |       | 25.51 | 19.9  |
|                |                  | <i>Fm-3m</i>      | 5.097 (10) | 132.4(8) | 28                 |                        |       |       |       |       |       |       |
| (CeSmPrZrTb)O₂ | LaY              | <i>Fm-3m</i>      | 5.272 (3)  | 146.3(3) | 74                 | 15.8                   |       | 21.53 | 16.89 |       | 22.69 | 23.09 |
|                |                  | <i>Fm-3m</i>      | 5.120 (13) | 134.2(9) | 26                 |                        |       |       |       |       |       |       |
| (LaSmPrZrTb)O₂ | CeY              | <i>Fm-3m</i>      | 5.248 (2)  | 144.5(2) | 60                 |                        | 18.55 | 20.42 | 18.54 |       | 23.17 | 19.32 |
|                |                  | <i>Fm-3m</i>      | 5.116 (6)  | 133.9(4) | 40                 |                        |       |       |       |       |       |       |
| (CeLaYZrTb)O₂  | SmPr             | <i>Fm-3m</i>      | 5.198 (4)  | 140.4(4) | 100                | 15.26                  | 16.54 |       |       | 22.24 | 26.71 | 19.26 |
| (CeSmYZrTb)O₂  | LaPr             | <i>Fm-3m</i>      | 5.236 (2)  | 143.3(2) | 100                | 15.25                  |       | 23.54 |       | 19.43 | 24.41 | 17.37 |

## Appendix

| Composition                   | Missing elements | Crystal structure            | a-axis (Å)             | V (Å <sup>3</sup> )  | Phase fraction (%) | Chemical concentration |       |       |       |       |       |       |
|-------------------------------|------------------|------------------------------|------------------------|----------------------|--------------------|------------------------|-------|-------|-------|-------|-------|-------|
|                               |                  |                              |                        |                      |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb    | Zr    |
| (LaSmYZrTb)O <sub>2</sub>     | CePr             | <i>Fm-3m</i><br><i>Fm-3m</i> | 5.146 (3)<br>5.132 (4) | 136.3(2)<br>135.2(4) | 93<br>7            |                        | 21.17 | 22.84 |       | 19.15 | 24.26 | 12.58 |
| (CePrYZrTb)O <sub>2</sub>     | LaSm             | <i>Fm-3m</i>                 | 5.212 (2)              | 141.6(2)             | 100                | 20.99                  |       |       | 17.3  | 20.9  | 20.2  | 20.61 |
| (LaPrYZrTb)O <sub>2</sub>     | CeSm             | <i>Fm-3m</i>                 | 5.717 (3)              | 138.3(2)             | 100                |                        | 15.67 |       | 15.24 | 22.78 | 23.71 | 22.6  |
| (SmPrYZrTb)O <sub>2</sub>     | CeLa             | <i>Fm-3m</i><br><i>Fm-3m</i> | 5.232 (2)<br>5.077 (2) | 143.2(2)<br>130.8(5) | 69<br>31           |                        |       | 21.96 | 19.93 | 21.51 | 20.44 | 16.16 |
| (CeLaSmPrYZr)O <sub>2</sub>   | Tb               | <i>Fm-3m</i>                 | 5.252 (3)              | 144.9(2)             | 100                | 17.07                  | 14.55 | 21.15 | 16.58 | 16.19 |       | 14.46 |
| (CeLaSmPrYTb)O <sub>2</sub>   | Zr               | <i>Fm-3m</i>                 | 5.254 (1)              | 145.0(1)             | 100                | 14.89                  | 15.27 | 17.47 | 14.13 | 21.43 | 16.82 |       |
| (CeLaSmPrZrTb)O <sub>2</sub>  | Y                | <i>Fm-3m</i>                 | 5.222 (2)              | 142.4(1)             | 100                | 16.25                  | 14.76 | 18.33 | 14.45 |       | 19.91 | 16.31 |
| (CeLaSmYZrTb)O <sub>2</sub>   | Pr               | <i>Fm-3m</i>                 | 5.226 (2)              | 142.7(1)             | 100                | 16.15                  | 15.24 | 17.15 |       | 14.03 | 22.91 | 14.55 |
| (CeLaPrYZrTb)O <sub>2</sub>   | Sm               | <i>Fm-3m</i>                 | 5.222 (2)              | 142.4(1)             | 100                | 16.57                  | 18.57 |       | 18.1  | 14.44 | 17.59 | 14.73 |
| (CeSmPrYZrTb)O <sub>2</sub>   | La               | <i>Fm-3m</i>                 | 5.260 (2)              | 145.6(2)             | 100                | 14.18                  |       | 18.12 | 16.66 | 14.64 | 21.17 | 15.22 |
| (LaSmPrYZrTb)O <sub>2</sub>   | Ce               | <i>Fm-3m</i>                 | 5.213 (2)              | 141.7(1)             | 100                | 14.34                  |       | 16.4  | 15.55 | 15.76 | 18.83 | 19.13 |
| (CeLaSmPrYZrTb)O <sub>2</sub> |                  | <i>Fm-3m</i>                 | 5.240 (2)              | 143.9(2)             | 100                | 14.19                  | 15.41 | 15.56 | 14.23 | 12.03 | 16.28 | 12.3  |

# Appendix

Table 15: Chemical composition and crystal structure parameters for the 64 rare earth fluorite-type structure oxides calcined at 900 °C.

| Composition              | Missing elements | Crystal structure     | a-axis (Å) | V (Å³)   | Phase fraction (%) | Chemical concentration |       |       |       |       |      |      |
|--------------------------|------------------|-----------------------|------------|----------|--------------------|------------------------|-------|-------|-------|-------|------|------|
|                          |                  |                       |            |          |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb   | Zr   |
| (CeLaSmPr)O <sub>2</sub> | TbYZr            | <i>Fm</i> −3 <i>m</i> | 5.389 (1)  | 156.5(1) | 100                | 24.11                  | 24.91 | 27.36 | 23.63 |       |      |      |
| (CeLaSmY)O <sub>2</sub>  | TbPrZr           | <i>Ia</i> −3          |            |          | 100                | 25.65                  | 24.01 | 26.87 |       | 23.47 |      |      |
| (CeLaPrY)O <sub>2</sub>  | SmTbZr           | <i>Fm</i> −3 <i>m</i> | 5.358 (1)  | 153.8(1) | 100                | 24.94                  | 24.62 |       | 22.33 | 28.11 |      |      |
| (CeSmPrY)O <sub>2</sub>  | LaTbZr           | <i>Fm</i> −3 <i>m</i> | 5.307 (1)  | 149.5(1) | 100                | 21.79                  |       | 25.74 | 22.24 | 30.23 |      |      |
| (LaSmPrY)O <sub>2</sub>  | CeTbZr           | <i>Ia</i> −3          |            |          | 100                |                        | 23.8  | 25.27 | 20.69 | 30.24 |      |      |
| (LaSmPrZr)O <sub>2</sub> | CeTbY            | <i>Fm</i> −3 <i>m</i> | 5.304 (1)  | 149.5(1) | 100                |                        | 26.5  | 25.2  | 25.1  |       |      | 23.2 |
| (CeLaSmZr)O <sub>2</sub> | PrTbY            | <i>Fm</i> −3 <i>m</i> | 5.336 (2)  | 151.9(1) | 49                 | 25.7                   | 24    | 25.1  |       |       |      | 25.2 |
|                          |                  | <i>Fm</i> −3 <i>m</i> | 5.129 (4)  | 134.9(3) | 51                 |                        |       |       |       |       |      |      |
| (CeLaPrZr)O <sub>2</sub> | SmTbY            | <i>Fm</i> −3 <i>m</i> | 5.378 (3)  | 155.5(3) | 76                 | 24.7                   | 24.6  |       | 22.3  |       |      | 28.3 |
|                          |                  | <i>Fm</i> −3 <i>m</i> | 5.512 (1)  | 167.4(1) | 37                 |                        |       |       |       |       |      |      |
| (CeSmPrZr)O <sub>2</sub> | LaTbY            | <i>Fm</i> −3 <i>m</i> | 5.267 (1)  | 146.1(1) | 100                | 25.4                   |       | 24.8  | 24.7  |       |      | 25.1 |
| (CePrZrTb)O <sub>2</sub> | LaSmY            | <i>Fm</i> −3 <i>m</i> | 5.241 (1)  | 144.0(1) | 81                 | 23.8                   |       |       | 23.2  |       | 25.1 | 27.9 |
|                          |                  | <i>Fm</i> −3 <i>m</i> | 5.137 (3)  | 135.6(2) | 19                 |                        |       |       |       |       |      |      |

## Appendix

| Composition              | Missing elements | Crystal structure | a-axis (Å) | V (Å <sup>3</sup> ) | Phase fraction (%) | Chemical concentration |       |       |       |       |       |       |
|--------------------------|------------------|-------------------|------------|---------------------|--------------------|------------------------|-------|-------|-------|-------|-------|-------|
|                          |                  |                   |            |                     |                    | Ce                     | La    | Sm    | Pr    | Y     | Tb    | Zr    |
| (CeLaYZr)O <sub>2</sub>  | SmPrTb           | <i>Fm-3m</i>      | 5.268 (1)  | 146.2(1)            | 100                | 22.8                   | 25.4  |       |       | 26.6  |       | 25.2  |
| (CeSmYZr)O <sub>2</sub>  | LaPrTb           | <i>Fm-3m</i>      | 5.219 (1)  | 142.1(1)            | 100                | 25.2                   | 24.5  |       |       | 30.2  |       | 20.1  |
| (LaSmYZr)O <sub>2</sub>  | CePrTb           | <i>Fm-3m</i>      | 5.253 (2)  | 145.0(2)            | 100                |                        | 27    | 24.7  |       | 27.3  |       | 21    |
| (CePrYZr)O <sub>2</sub>  | LaSmTb           | <i>Fm-3m</i>      | 5.242 (1)  | 144.0(1)            | 83                 | 25.1                   |       |       | 26.6  | 24.9  |       | 23.4  |
|                          |                  | <i>Fm-3m</i>      | 5.133 (2)  | 135.3(2)            | 17                 |                        |       |       |       |       |       |       |
| (LaPrYZr)O <sub>2</sub>  | CeSmTb           | <i>Fm-3m</i>      | 5.285 (3)  | 147.7(2)            | 85                 |                        | 24.36 |       | 24.86 | 26.17 |       | 24.61 |
|                          |                  | <i>Fm-3m</i>      | 5.263 (2)  | 145.8(1)            | 15                 |                        |       |       |       |       |       |       |
| (SmPrYZr)O <sub>2</sub>  | CeLaTb           | <i>Fm-3m</i>      | 5.234 (1)  | 143.4(1)            | 100                |                        |       | 25.96 | 24.6  | 24.19 |       | 25.25 |
| (CeLaSmTb)O <sub>2</sub> | PrYZr            | <i>Fm-3m</i>      | 5.344 (1)  | 152.6(1)            | 100                | 22.67                  | 23.62 | 27.57 |       |       | 26.14 |       |
| (CeLaPrTb)O <sub>2</sub> | SmYZr            | <i>Fm-3m</i>      | 5.344 (1)  | 152.6(1)            | 62                 | 27.5                   | 26    |       | 24.4  |       | 22.1  |       |
|                          |                  | <i>Fm-3m</i>      | 5.224 (2)  | 142.6(1)            | 38                 |                        |       |       |       |       |       |       |
| (CeSmPrTb)O <sub>2</sub> | LaYZr            | <i>Fm-3m</i>      | 5.283 (1)  | 147.5(1)            | 100                | 23.44                  |       | 27.77 | 22.01 |       | 26.77 |       |
| (LaSmPrTb)O <sub>2</sub> | CeYZr            | <i>Fm-3m</i>      | 5.354 (1)  | 153.5(1)            | 100                |                        | 21.59 | 27.44 | 21.41 | 29.57 |       |       |
| (CeLaYTb)O <sub>2</sub>  | SmPrZr           | <i>Fm-3m</i>      | 5.309 (1)  | 149.6(1)            | 100                | 25.63                  | 26.67 |       |       | 25.97 | 21.73 |       |

## Appendix

| Composition              | Missing elements | Crystal structure     | a-axis (Å) | V (Å³)    | Phase fraction (%) | Chemical concentration |       |      |       |      |       |       |
|--------------------------|------------------|-----------------------|------------|-----------|--------------------|------------------------|-------|------|-------|------|-------|-------|
|                          |                  |                       |            |           |                    | Ce                     | La    | Sm   | Pr    | Y    | Tb    | Zr    |
| (CeSmYTb)O <sub>2</sub>  | LaPrZr           | <i>Ia</i> -3          | 10.515 (1) | 1162.5(3) | 100                | 25.9                   |       | 24.7 |       | 26.6 | 22.8  |       |
| (LaSmYTb)O <sub>2</sub>  | CePrZr           | Multi                 |            |           |                    |                        | 24.1  | 23   |       | 27.3 | 25.7  |       |
| (CePrYTb)O <sub>2</sub>  | LaSmZr           | <i>Fm</i> -3 <i>m</i> | 5.256 (1)  | 145.2(1)  | 100                | 25.2                   |       |      | 24.3  | 27   | 23.5  |       |
| (LaPrYTb)O <sub>2</sub>  | CeSmZr           | <i>Fm</i> -3 <i>m</i> | 5.357 (2)  | 153.8(1)  | 74                 |                        | 28    |      | 22.6  | 25.1 | 24.3  |       |
|                          |                  | <i>Fm</i> -3 <i>m</i> | 5.251 (3)  | 144.8(2)  | 26                 |                        |       |      |       |      |       |       |
| (SmPrYTb)O <sub>2</sub>  | CeLaZr           | <i>Ia</i> -3          | 10.531 (1) | 1167.8(4) | 100                |                        |       | 22.9 | 24.5  | 26.2 | 26.4  |       |
| (CeLaZrTb)O <sub>2</sub> | SmPrY            | <i>Fm</i> -3 <i>m</i> | 5.273 (1)  | 153.8(1)  | 100                | 24.7                   | 25.3  |      |       |      | 26.3  | 23.7  |
| (CeSmZrTb)O <sub>2</sub> | LaPrY            | <i>Fm</i> -3 <i>m</i> | 5.225 (1)  | 142.6(1)  | 89                 | 21.1                   |       | 26.3 |       |      | 27.1  | 25.5  |
|                          |                  | <i>Fm</i> -3 <i>m</i> | 5.103 (3)  | 132.8(2)  | 11                 |                        |       |      |       |      |       |       |
| (LaSmZrTb)O <sub>2</sub> | CePrY            | <i>Fm</i> -3 <i>m</i> | 5.261 (1)  | 145.6(1)  | 100                |                        | 23.5  | 27   |       |      | 28.7  | 20.8  |
| (LaPrZrTb)O <sub>2</sub> | CeSmY            | <i>Fm</i> -3 <i>m</i> | 5.276 (1)  | 146.9(1)  | 100                |                        | 23.34 |      | 25.81 |      | 24.89 | 25.95 |
| (SmPrZrTb)O <sub>2</sub> | CeLaY            | <i>Fm</i> -3 <i>m</i> | 5.229 (1)  | 142.9(1)  | 88                 |                        |       | 24   | 18.5  | 28.1 | 29.5  |       |
|                          |                  | <i>Fm</i> -3 <i>m</i> | 5.118 (3)  | 134.0(2)  | 12                 |                        |       |      |       |      |       |       |
| (CeYZrTb)O <sub>2</sub>  | LaSmPr           | <i>Fm</i> -3 <i>m</i> | 5.181 (1)  | 139.1(1)  | 100                | 23.5                   |       |      |       | 26   | 25.9  | 24.7  |

## Appendix

| Composition                | Missing elements | Crystal structure     | a-axis (Å) | V (Å³)    | Phase fraction (%) | Chemical concentration |      |      |      |      |      |      |
|----------------------------|------------------|-----------------------|------------|-----------|--------------------|------------------------|------|------|------|------|------|------|
|                            |                  |                       |            |           |                    | Ce                     | La   | Sm   | Pr   | Y    | Tb   | Zr   |
| (LaYZrTb)O <sub>2</sub>    | CeSmPr           | <i>Fm</i> −3 <i>m</i> | 5.203 (2)  | 140.9(1)  | 100                |                        | 22.1 |      |      | 25.9 | 24.4 | 27.6 |
| (SmYZrTb)O <sub>2</sub>    | CeLaPr           | <i>Fm</i> −3 <i>m</i> | 5.186 (1)  | 139.5(1)  | 100                |                        |      | 23.6 |      | 25.5 | 25.7 | 25.3 |
| (PrYZrTb)O <sub>2</sub>    | CeLaSm           | <i>Fm</i> −3 <i>m</i> | 5.198 (1)  | 140.5(1)  | 100                |                        |      |      | 24.3 | 26.3 | 23.3 | 26.2 |
| (CeLaSmPrY)O <sub>2</sub>  | TbZr             | <i>Ia</i> −3          | 10.737 (1) | 1237.7(3) | 100                | 20.1                   | 22.1 | 19.6 | 18   | 20.2 |      |      |
| (CeLaSmPrZr)O <sub>2</sub> | TbY              | <i>Fm</i> −3 <i>m</i> | 5.316 (1)  | 150.2(1)  | 100                | 20.8                   | 22.3 | 17.1 | 18.5 |      |      | 21.4 |
| (CeLaSmYZr)O <sub>2</sub>  | PrTb             | <i>Fm</i> −3 <i>m</i> | 5.300 (2)  | 148.9(2)  | 86                 | 19.5                   | 20.2 |      | 20.4 | 20.4 |      | 19.5 |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.123 (3)  | 134.4(2)  | 14                 |                        |      |      |      |      |      |      |
| (CeLaPrYZr)O <sub>2</sub>  | SmTb             | <i>Fm</i> −3 <i>m</i> | 5.321(1)   | 150.7(1)  | 51                 | 19.9                   | 22.4 |      | 17.8 | 20.9 |      | 19.9 |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.178 (2)  | 138.9(2)  | 49                 |                        |      |      |      |      |      |      |
| (CeSmPrYZr)O <sub>2</sub>  | LaTb             | <i>Fm</i> −3 <i>m</i> | 5.256 (1)  | 145.2(1)  | 100                | 19.1                   |      | 18.7 | 19.9 | 21.5 |      | 20.9 |
| (LaSmPrYZr)O <sub>2</sub>  | CeTb             | <i>Fm</i> −3 <i>m</i> | 5.302 (1)  | 149.0(1)  | 100                |                        | 24.5 | 20   | 21.9 | 16.2 |      | 17.5 |
| (CeLaSmPrTb)O <sub>2</sub> | YZr              | <i>Fm</i> −3 <i>m</i> | 5.347 (1)  | 152.9(1)  | 92                 | 21.2                   | 22.8 | 19.8 | 19.3 |      | 16.9 |      |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.234 (2)  | 143.4(2)  | 8                  |                        |      |      |      |      |      |      |
| (CeLaSmYTb)O <sub>2</sub>  | PrZr             | <i>Fm</i> −3 <i>m</i> | 5.320 (1)  | 150.6(1)  | 100                | 20.4                   | 20.4 | 20.8 |      | 21.4 | 16.9 |      |



## Appendix

| Composition                | Missing elements | Crystal structure     | a-axis (Å) | V (Å³)   | Phase fraction (%) | Chemical concentration |      |       |      |      |       |       |
|----------------------------|------------------|-----------------------|------------|----------|--------------------|------------------------|------|-------|------|------|-------|-------|
|                            |                  |                       |            |          |                    | Ce                     | La   | Sm    | Pr   | Y    | Tb    | Zr    |
| (CeLaPrYTb)O <sub>2</sub>  | SmZr             | <i>Fm</i> −3 <i>m</i> | 5.316 (1)  | 150.2(1) | 100                | 19.8                   | 19.2 |       | 19.8 | 21.9 | 19.4  |       |
| (CeSmPrYTb)O <sub>2</sub>  | LaZr             | <i>Fm</i> −3 <i>m</i> | 5.283 (1)  | 147.4(1) | 100                | 19.6                   |      | 19.3  | 19.1 | 21.7 | 20.2  |       |
| (LaSmPrYTb)O <sub>2</sub>  | CeZr             | <i>Fm</i> −3 <i>m</i> | 5.336 (1)  | 151.9(1) | 100                |                        | 19.7 | 17.4  | 21.1 | 20.7 | 21.2  |       |
| (CeLaSmZrTb)O <sub>2</sub> | PrY              | <i>Fm</i> −3 <i>m</i> | 5.301 (3)  | 148.9(3) | 73                 | 19.7                   | 17.4 | 21.1  |      |      | 21.2  | 20.7  |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.129 (6)  | 134.9(5) | 27                 |                        |      |       |      |      |       |       |
| (CeLaPrZrTb)O <sub>2</sub> | SmY              | <i>Fm</i> −3 <i>m</i> | 5.289 (1)  | 147.9(1) | 100                | 19.1                   | 15.8 |       | 17   |      | 23.5  | 24.6  |
| (CeSmPrZrTb)O <sub>2</sub> | LaY              | <i>Fm</i> −3 <i>m</i> | 5.257 (1)  | 145.2(1) | 57                 | 18.31                  |      | 19.21 | 18.1 |      | 19.94 | 24.44 |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.176 (3)  | 138.7(3) | 43                 |                        |      |       |      |      |       |       |
| (LaSmPrZrTb)O <sub>2</sub> | CeY              | <i>Fm</i> −3 <i>m</i> | 5.287 (1)  | 147.8(1) | 100                |                        | 18.9 | 18.8  | 18.4 |      | 19.1  | 24.8  |
| (CeLaYZrTb)O <sub>2</sub>  | SmPr             | <i>Fm</i> −3 <i>m</i> | 5.395 (4)  | 157.0(3) | 24                 | 18.4                   | 21.1 |       |      | 21.8 | 17.6  | 21.2  |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.219 (3)  | 142.2(3) | 76                 |                        |      |       |      |      |       |       |
| (CeSmYZrTb)O <sub>2</sub>  | LaPr             | <i>Fm</i> −3 <i>m</i> | 5.219 (1)  | 142.2(1) | 80                 | 17.8                   |      | 18    |      | 22.3 | 17.5  | 24.4  |
|                            |                  | <i>Fm</i> −3 <i>m</i> | 5.122 (3)  | 134.4(2) | 20                 |                        |      |       |      |      |       |       |

| Composition                   | Missing elements | Crystal structure            | a-axis (Å)             | V (Å <sup>3</sup> )  | Phase fraction (%) | Chemical concentration |      |      |      |      |      |      |
|-------------------------------|------------------|------------------------------|------------------------|----------------------|--------------------|------------------------|------|------|------|------|------|------|
|                               |                  |                              |                        |                      |                    | Ce                     | La   | Sm   | Pr   | Y    | Tb   | Zr   |
| (LaSmYZrTb)O <sub>2</sub>     | CePr             | <i>Fm-3m</i><br><i>Fm-3m</i> | 5.263 (2)<br>5.133 (5) | 145.8(1)<br>135.2(4) | 89<br>11           |                        | 18.7 | 18.2 |      | 21.5 |      | 22.4 |
| (CePrYZrTb)O <sub>2</sub>     | LaSm             | <i>Fm-3m</i>                 | 5.240 (1)              | 143.9(1)             | 100                | 16.4                   |      |      | 16.8 | 22.8 | 19.1 | 24.2 |
| (LaPrYZrTb)O <sub>2</sub>     | CeSm             | <i>Fm-3m</i>                 | 5.239 (1)              | 143.8(1)             | 100                |                        | 19.4 |      | 17.5 | 20.1 | 18.5 | 24.5 |
| (SmPrYZrTb)O <sub>2</sub>     | CeLa             | <i>Fm-3m</i><br><i>Fm-3m</i> | 5.247 (2)<br>5.157 (5) | 144.5(2)<br>137.2(4) | 68<br>32           |                        |      | 20.1 | 14.2 | 22.7 | 20.4 | 22.6 |
| (CeLaSmPrYZr)O <sub>2</sub>   | Tb               | <i>Fm-3m</i>                 | 5.309 (2)              | 149.7(2)             | 100                | 15.5                   | 14.5 | 14.4 | 16.2 | 17.8 |      | 21.6 |
| (CeLaSmPrYTb)O <sub>2</sub>   | Zr               | <i>Fm-3m</i>                 | 5.323 (1)              | 150.9(1)             | 100                | 16.6                   | 17.6 | 16.7 | 15.9 | 18.5 | 14.7 |      |
| (CeLaSmPrZrTb)O <sub>2</sub>  | Y                | <i>Fm-3m</i>                 | 5.303 (1)              | 149.2(1)             | 100                | 17.4                   | 18.9 | 15.4 | 15.5 |      | 14.1 | 18.7 |
| (CeLaSmYZrTb)O <sub>2</sub>   | Pr               | <i>Fm-3m</i>                 | 5.271 (2)              | 146.4(1)             | 100                | 16.1                   | 17.7 | 15.4 |      | 17.5 | 16.1 | 17.2 |
| (CeLaPrYZrTb)O <sub>2</sub>   | Sm               | <i>Fm-3m</i>                 | 5.282 (1)              | 147.4 (1)            | 100                | 15.1                   | 14.5 |      | 15.2 | 18.1 | 17   | 20.1 |
| (CeSmPrYZrTb)O <sub>2</sub>   | La               | <i>Fm-3m</i>                 | 5.251 (1)              | 144.8 (1)            | 100                | 14.4                   |      | 13.8 | 13.1 | 18.2 | 15   | 25.5 |
| (LaSmPrYZrTb)O <sub>2</sub>   | Ce               | <i>Fm-3m</i>                 | 5.309 (1)              | 149.7 (1)            | 100                |                        | 16.9 | 14.1 | 14.7 | 14.9 | 17.7 | 21.7 |
| (CeLaSmPrYZrTb)O <sub>2</sub> |                  | <i>Fm-3m</i>                 | 5.290 (1)              | 147.7 (1)            | 100                | 14.3                   | 14.3 | 14.3 | 13.4 | 15.5 | 13.6 | 14.6 |

*Table 16: Comparison of direct band gap energies for different medium- and high-entropy fluorite-type oxides calcined at 700 °C and 900 °C.*

| <b>Composition</b>       | <b>Band gap energy at 700 °C - air</b> | <b>Band gap energy at 900°C - air</b> |
|--------------------------|----------------------------------------|---------------------------------------|
| (CeLaSmPr)O <sub>2</sub> | 2.08                                   | 2.06                                  |
| (CeLaSmY)O <sub>2</sub>  | 3.37                                   | 3.35                                  |
| (CeLaPrY)O <sub>2</sub>  | 2.1                                    | 2.05                                  |
| (CeSmPrY)O <sub>2</sub>  | 2.08                                   | 3.26                                  |
| (LaSmPrY)O <sub>2</sub>  | 2                                      | 2.14                                  |
| (LaSmPrZr)O <sub>2</sub> | 2.22                                   | 2.02                                  |
| (CeLaSmZr)O <sub>2</sub> | 3.36                                   | 3.22                                  |
| (CeLaPrZr)O <sub>2</sub> | 2.09                                   | 2.1                                   |
| (CeSmPrZr)O <sub>2</sub> | 2.1                                    | 1.91                                  |
| (CePrZrTb)O <sub>2</sub> | 2.16                                   | 1.88                                  |
| (CeLaYZr)O <sub>2</sub>  | 3.41                                   | 3.33                                  |
| (CeSmYZr)O <sub>2</sub>  | 3.35                                   | 3.29                                  |
| (LaSmYZr)O <sub>2</sub>  | 4.91                                   | 3.03                                  |
| (CePrYZr)O <sub>2</sub>  | 2.12                                   | 1.84                                  |
| (LaPrYZr)O <sub>2</sub>  | 2.15                                   | 2.08                                  |
| (SmPrYZr)O <sub>2</sub>  | 2.14                                   | 2.02                                  |
| (CeLaSmTb)O <sub>2</sub> | 2.14                                   | 2.14                                  |
| (CeLaPrTb)O <sub>2</sub> | 1.99                                   | 2.05                                  |
| (CeSmPrTb)O <sub>2</sub> | 1.92                                   | 2.06                                  |
| (LaSmPrTb)O <sub>2</sub> | 2.05                                   | 2.23                                  |
| (CeLaYTb)O <sub>2</sub>  | 2.08                                   | 2.14                                  |
| (CeSmYTb)O <sub>2</sub>  | 2.14                                   | 2.13                                  |
| (LaSmYTb)O <sub>2</sub>  | 2.25                                   | 2.24                                  |

| Composition                | Band gap energy at 700 °C - air | Band gap energy at 900°C - air |
|----------------------------|---------------------------------|--------------------------------|
| (CePrYTb)O <sub>2</sub>    | 1.95                            | 2.02                           |
| (LaPrYTb)O <sub>2</sub>    | 2.13                            | 2.14                           |
| (SmPrYTb)O <sub>2</sub>    | 2.01                            | 2.11                           |
| (CeLaZrTb)O <sub>2</sub>   | 2.22                            | 2.11                           |
| (CeSmZrTb)O <sub>2</sub>   | 2.25                            | 2.06                           |
| (LaSmZrTb)O <sub>2</sub>   | 2.11                            | 2.14                           |
| (LaPrZrTb)O <sub>2</sub>   | 2.11                            | 1.96                           |
| (SmPrZrTb)O <sub>2</sub>   | 2.12                            | 1.99                           |
| (CeYZrTb)O <sub>2</sub>    | 2.25                            | 2.07                           |
| (LaYZrTb)O <sub>2</sub>    | 2.24                            | 2.22                           |
| (SmYZrTb)O <sub>2</sub>    | 2.31                            | 2.06                           |
| (PrYZrTb)O <sub>2</sub>    | 2.18                            | 2.03                           |
| (CeLaSmPrY)O <sub>2</sub>  | 1.99                            | 2.12                           |
| (CeLaSmPrZr)O <sub>2</sub> | 2.06                            | 1.97                           |
| (CeLaSmYZr)O <sub>2</sub>  | 3.36                            | 3.31                           |
| (CeLaPrYZr)O <sub>2</sub>  | 2.2                             | 2.02                           |
| (CeSmPrYZr)O <sub>2</sub>  | 2.21                            | 2.01                           |
| (LaSmPrYZr)O <sub>2</sub>  | 2.14                            | 2.09                           |
| (CeLaSmPrTb)O <sub>2</sub> | 2.08                            | 2.09                           |
| (CeLaSmYTb)O <sub>2</sub>  | 2.13                            | 2.22                           |
| (CeLaPrYTb)O <sub>2</sub>  | 2.06                            | 2.17                           |
| (CeSmPrYTb)O <sub>2</sub>  | 2.05                            | 2.14                           |
| (LaSmPrYTb)O <sub>2</sub>  | 2.11                            | 2.24                           |
| (CeLaSmZrTb)O <sub>2</sub> | 2.18                            | 2.14                           |

| Composition                   | Band gap energy at 700 °C - air | Band gap energy at 900°C - air |
|-------------------------------|---------------------------------|--------------------------------|
| (CeLaPrZrTb)O <sub>2</sub>    | 2.17                            | 2.02                           |
| (CeSmPrZrTb)O <sub>2</sub>    | 2.24                            | 2.04                           |
| (LaSmPrZrTb)O <sub>2</sub>    | 2.16                            | 2.02                           |
| (CeLaYZrTb)O <sub>2</sub>     | 2.24                            | 2.17                           |
| (CeSmYZrTb)O <sub>2</sub>     | 2.26                            | 2.17                           |
| (LaSmYZrTb)O <sub>2</sub>     | 2.19                            | 2.21                           |
| (CePrYZrTb)O <sub>2</sub>     | 2.22                            | 1.98                           |
| (LaPrYZrTb)O <sub>2</sub>     | 2.08                            | 2.07                           |
| (SmPrYZrTb)O <sub>2</sub>     | 2.19                            | 1.94                           |
| (CeLaSmPrYZr)O <sub>2</sub>   | 2.18                            | 2.08                           |
| (CeLaSmPrYTb)O <sub>2</sub>   | 2.09                            | 2.1                            |
| (CeLaSmPrZrTb)O <sub>2</sub>  | 2.19                            | 2                              |
| (CeLaSmYZrTb)O <sub>2</sub>   | 2.22                            | 2.15                           |
| (CeLaPrYZrTb)O <sub>2</sub>   | 2.18                            | 2.01                           |
| (CeSmPrYZrTb)O <sub>2</sub>   | 2.23                            | 1.96                           |
| (LaSmPrYZrTb)O <sub>2</sub>   | 2.1                             | 2.18                           |
| (CeLaSmPrYZrTb)O <sub>2</sub> | 2.2                             | 2.17                           |

Table 17: Comparison of band gap energies after calcination in different atmospheres at 700 °C.

| Composition              | Band gap energy at 700 °C – air | Band gap energy at 700 °C – argon | Band gap energy at 700 °C – 10% H <sub>2</sub> + argon | Band gap energy at 700 °C – air |
|--------------------------|---------------------------------|-----------------------------------|--------------------------------------------------------|---------------------------------|
| (CeLaSmPr)O <sub>2</sub> | 2.08                            | 3.25                              | 2.51                                                   | 2.01                            |
| (CeLaSmY)O <sub>2</sub>  | 3.37                            | 3.34                              | 3.35                                                   | 3.36                            |
| (CeLaPrY)O <sub>2</sub>  | 2.1                             | 3.34                              | 2.19                                                   | 2.14                            |
| (CeSmPrY)O <sub>2</sub>  | 2.08                            | 3.26                              | 2.19                                                   | 2.08                            |
| (LaSmPrY)O <sub>2</sub>  | 2                               | 3.4                               | 3.46                                                   | 1.99                            |
| (LaSmPrZr)O <sub>2</sub> | 2.22                            | 3.45                              | 3.22                                                   | 2.13                            |
| (CeLaSmZr)O <sub>2</sub> | 3.36                            | 3.34                              | 3.32                                                   | 3.36                            |
| (CeLaPrZr)O <sub>2</sub> | 2.09                            | 3.25                              | 3.26                                                   | 2.3                             |
| (CeSmPrZr)O <sub>2</sub> | 2.1                             | 3.19                              | 3.14                                                   | 2.09                            |
| (CePrZrTb)O <sub>2</sub> | 2.16                            | 2.29                              | 2.16                                                   | 2.07                            |
| (CeLaYZr)O <sub>2</sub>  | 3.41                            | 3.34                              | 3.3                                                    | 3.34                            |
| (CeSmYZr)O <sub>2</sub>  | 3.35                            | 3.28                              | 3.28                                                   | 3.32                            |
| (LaSmYZr)O <sub>2</sub>  | 4.91                            | 4.78                              | 4.76                                                   | 4.89                            |
| (CePrYZr)O <sub>2</sub>  | 2.12                            | 2.31                              | 2.09                                                   | 2.11                            |
| (LaPrYZr)O <sub>2</sub>  | 2.15                            | 3.38                              | 3.22                                                   | 2.07                            |
| (SmPrYZr)O <sub>2</sub>  | 2.14                            | 3.3                               | 3.47                                                   | 2.21                            |
| (CeLaSmTb)O <sub>2</sub> | 2.14                            | 3.3                               | 3.23                                                   | 2.09                            |
| (CeLaPrTb)O <sub>2</sub> | 1.99                            | 2.43                              | 2.29                                                   | 2.02                            |
| (CeSmPrTb)O <sub>2</sub> | 1.92                            | 2.49                              | 2.18                                                   | 1.94                            |
| (LaSmPrTb)O <sub>2</sub> | 2.05                            | 3.44                              | 3.5                                                    | 2.02                            |
| (CeLaYTb)O <sub>2</sub>  | 2.08                            | 3.31                              | 2.34                                                   | 2.06                            |
| (CeSmYTb)O <sub>2</sub>  | 2.14                            | 3.3                               | 3.25                                                   | 2.1                             |
| (LaSmYTb)O <sub>2</sub>  | 2.25                            | 3.64                              | 3.53                                                   | 2.33                            |

| <b>Composition</b>         | <b>Band gap energy<br/>at 700 °C – air</b> | <b>Band gap energy<br/>at 700 °C – argon</b> | <b>Band gap energy<br/>at 700 °C – 10% H<sub>2</sub><br/>+ argon</b> | <b>Band gap energy<br/>at 700 °C – air</b> |
|----------------------------|--------------------------------------------|----------------------------------------------|----------------------------------------------------------------------|--------------------------------------------|
| (CePrYTb)O <sub>2</sub>    | 1.95                                       | 2.48                                         | 2.4                                                                  | 1.99                                       |
| (LaPrYTb)O <sub>2</sub>    | 2.13                                       | 3.42                                         | 3.53                                                                 | 2.16                                       |
| (SmPrYTb)O <sub>2</sub>    | 2.01                                       | 3.5                                          | 3.51                                                                 | 1.99                                       |
| (CeLaZrTb)O <sub>2</sub>   | 2.22                                       | 3.37                                         | 3.29                                                                 | 2.3                                        |
| (CeSmZrTb)O <sub>2</sub>   | 2.25                                       | 3.25                                         | 3.19                                                                 | 2.21                                       |
| (LaSmZrTb)O <sub>2</sub>   | 2.11                                       | 3.43                                         | 3.35                                                                 | 2.09                                       |
| (LaPrZrTb)O <sub>2</sub>   | 2.11                                       | 3.23                                         | 3.06                                                                 | 2.06                                       |
| (SmPrZrTb)O <sub>2</sub>   | 2.12                                       | 3.26                                         | 3.07                                                                 | 2.01                                       |
| (CeYZrTb)O <sub>2</sub>    | 2.25                                       | 3.37                                         | 3.28                                                                 | 2.25                                       |
| (LaYZrTb)O <sub>2</sub>    | 2.24                                       | 3.49                                         | 3.14                                                                 | 2.22                                       |
| (SmYZrTb)O <sub>2</sub>    | 2.31                                       | 3.39                                         | 2.72                                                                 | 2.2                                        |
| (PrYZrTb)O <sub>2</sub>    | 2.18                                       | 3.37                                         | 2.98                                                                 | 2.12                                       |
| (CeLaSmPrY)O <sub>2</sub>  | 1.99                                       | 3.35                                         | 3.33                                                                 | 2.05                                       |
| (CeLaSmPrZr)O <sub>2</sub> | 2.06                                       | 3.28                                         | 3.29                                                                 | 2.15                                       |
| (CeLaSmYZr)O <sub>2</sub>  | 3.36                                       | 3.32                                         | 3.22                                                                 | 3.32                                       |
| (CeLaPrYZr)O <sub>2</sub>  | 2.2                                        | 3.24                                         | 2.52                                                                 | 2.21                                       |
| (CeSmPrYZr)O <sub>2</sub>  | 2.21                                       | 3.36                                         | 3.29                                                                 | 2.12                                       |
| (LaSmPrYZr)O <sub>2</sub>  | 2.14                                       | 3.41                                         | 3.11                                                                 | 2.06                                       |
| (CeLaSmPrTb)O <sub>2</sub> | 2.08                                       | 2.52                                         | 2.25                                                                 | 2.08                                       |
| (CeLaSmYTb)O <sub>2</sub>  | 2.13                                       | 3.27                                         | 3.03                                                                 | 2.12                                       |
| (CeLaPrYTb)O <sub>2</sub>  | 2.06                                       | 2.35                                         | 2.05                                                                 | 2.05                                       |
| (CeSmPrYTb)O <sub>2</sub>  | 2.05                                       | 3.33                                         | 3.26                                                                 | 1.97                                       |
| (LaSmPrYTb)O <sub>2</sub>  | 2.11                                       | 3.51                                         | 3.49                                                                 | 2.1                                        |
| (CeLaSmZrTb)O <sub>2</sub> | 2.18                                       | 3.25                                         | 3.11                                                                 | 2.13                                       |

| <b>Composition</b>                | <b>Band gap energy<br/>at 700 °C – air</b> | <b>Band gap energy<br/>at 700 °C – argon</b> | <b>Band gap energy<br/>at 700 °C – 10% H<sub>2</sub><br/>+ argon</b> | <b>Band gap energy<br/>at 700 °C – air</b> |
|-----------------------------------|--------------------------------------------|----------------------------------------------|----------------------------------------------------------------------|--------------------------------------------|
| (CeLaPrZrTb)O <sub>2</sub>        | 2.17                                       | 2.43                                         | 2.23                                                                 | 2.13                                       |
| (CeSmPrZrTb)O <sub>2</sub>        | 2.24                                       | 2.42                                         | 2.15                                                                 | 2.26                                       |
| (LaSmPrZrTb)O <sub>2</sub>        | 2.16                                       | 3.44                                         | 3.18                                                                 | 2.12                                       |
| (CeLaYZrTb)O <sub>2</sub>         | 2.24                                       | 3.28                                         | 3.25                                                                 | 2.31                                       |
| (CeSmYZrTb)O <sub>2</sub>         | 2.26                                       | 3.3                                          | 3.22                                                                 | 2.29                                       |
| (LaSmYZrTb)O <sub>2</sub>         | 2.19                                       | 3.49                                         | 3.17                                                                 | 2.09                                       |
| (CePrYZrTb)O <sub>2</sub>         | 2.22                                       | 2.39                                         | 2.12                                                                 | 2.16                                       |
| (LaPrYZrTb)O <sub>2</sub>         | 2.08                                       | 3.45                                         | 3                                                                    | 2.04                                       |
| (SmPrYZrTb)O <sub>2</sub>         | 2.19                                       | 3.44                                         | 3.01                                                                 | 2.12                                       |
| (CeLaSmPrYZr)O <sub>2</sub>       | 2.18                                       | 3.32                                         | 3.2                                                                  | 2.22                                       |
| (CeLaSmPrYTb)O <sub>2</sub>       | 2.09                                       | 2.61                                         | 2.49                                                                 | 2.03                                       |
| (CeLaSmPrZrTb)O <sub>2</sub>      | 2.19                                       | 2.52                                         | 2.24                                                                 | 2.18                                       |
| (CeLaSmYZrTb)O <sub>2</sub>       | 2.22                                       | 3.26                                         | 3.25                                                                 | 2.31                                       |
| (CeLaPrYZrTb)O <sub>2</sub>       | 2.18                                       | 3.16                                         | 3.29                                                                 | 2.19                                       |
| (CeSmPrYZrTb)O <sub>2</sub>       | 2.23                                       | 3.27                                         | 3.21                                                                 | 2.2                                        |
| (LaSmPrYZrTb)O <sub>2</sub>       | 2.1                                        | 3.5                                          | 3.02                                                                 | 2.04                                       |
| (CeLaSmPrYZrTb)<br>O <sub>2</sub> | 2.2                                        | 3.28                                         | 3.22                                                                 | 2.24                                       |



Table 18: Comparison of band gap energies after calcination in different atmospheres at 900 °C.

| Composition              | Band gap energy at 900 °C – air | Band gap energy at 900 °C – argon | Band gap energy at 900 °C – 10% H <sub>2</sub> + argon | Band gap energy at 900 °C – air |
|--------------------------|---------------------------------|-----------------------------------|--------------------------------------------------------|---------------------------------|
| (CeLaSmPr)O <sub>2</sub> | 2.06                            | 3.36                              | 3.36                                                   | 3.18                            |
| (CeLaSmY)O <sub>2</sub>  | 3.35                            | 3.3                               | 3.41                                                   | 3.38                            |
| (CeLaPrY)O <sub>2</sub>  | 2.05                            | 3.41                              | 3.42                                                   | 2.22                            |
| (CeSmPrY)O <sub>2</sub>  | 3.26                            | 3.38                              | 3.41                                                   | 2.14                            |
| (LaSmPrY)O <sub>2</sub>  | 2.14                            | 3.41                              | 3.51                                                   | 2.17                            |
| (LaSmPrZr)O <sub>2</sub> | 2.02                            | 2.99                              | 3.26                                                   | 1.9                             |
| (CeLaSmZr)O <sub>2</sub> | 3.22                            | 3.33                              | 3.36                                                   | 3.42                            |
| (CeLaPrZr)O <sub>2</sub> | 2.1                             | 3.3                               | 3.36                                                   | 2.11                            |
| (CeSmPrZr)O <sub>2</sub> | 1.91                            | 2.25                              | 2.57                                                   | 2.05                            |
| (CePrZrTb)O <sub>2</sub> | 1.88                            | 2.33                              | 2.37                                                   | 3.2                             |
| (CeLaYZr)O <sub>2</sub>  | 3.33                            | 3.35                              | 3.39                                                   | 3.36                            |
| (CeSmYZr)O <sub>2</sub>  | 3.29                            | 3.32                              | 2.59                                                   | 3.3                             |
| (LaSmYZr)O <sub>2</sub>  | 3.03                            | 2.9                               | 2.93                                                   | 3.09                            |
| (CePrYZr)O <sub>2</sub>  | 1.84                            | 2.31                              | 3.39                                                   | 3.33                            |
| (LaPrYZr)O <sub>2</sub>  | 2.08                            | 3.43                              | 2.78                                                   | 2.1                             |
| (SmPrYZr)O <sub>2</sub>  | 2.02                            | 3.37                              | 3.14                                                   | 1.92                            |
| (CeLaSmTb)O <sub>2</sub> | 2.14                            | 3.42                              | 3.44                                                   | 2.27                            |
| (CeLaPrTb)O <sub>2</sub> | 2.05                            | 3.42                              | 3.43                                                   | 2.05                            |
| (CeSmPrTb)O <sub>2</sub> | 2.06                            | 3.37                              | 3.43                                                   | 2.15                            |
| (LaSmPrTb)O <sub>2</sub> | 2.23                            | 3.39                              | 3.52                                                   | 2.18                            |
| (CeLaYTb)O <sub>2</sub>  | 2.14                            | 3.36                              | 2.7                                                    | 2.18                            |
| (CeSmYTb)O <sub>2</sub>  | 2.13                            | 3.38                              | 3.4                                                    | 2.24                            |
| (LaSmYTb)O <sub>2</sub>  | 2.24                            | 3.37                              | 3.52                                                   | 2.27                            |

| <b>Composition</b>         | <b>Band gap energy<br/>at 900 °C – air</b> | <b>Band gap energy<br/>at 900 °C – argon</b> | <b>Band gap energy<br/>at 900 °C – 10% H<sub>2</sub><br/>+ argon</b> | <b>Band gap energy<br/>at 900 °C – air</b> |
|----------------------------|--------------------------------------------|----------------------------------------------|----------------------------------------------------------------------|--------------------------------------------|
| (CePrYTb)O <sub>2</sub>    | 2.02                                       | 3.32                                         | 3.37                                                                 | 3.24                                       |
| (LaPrYTb)O <sub>2</sub>    | 2.14                                       | 3.38                                         | 3.49                                                                 | 2.13                                       |
| (SmPrYTb)O <sub>2</sub>    | 2.11                                       | 3.4                                          | 3.51                                                                 | 2.17                                       |
| (CeLaZrTb)O <sub>2</sub>   | 2.11                                       | 3.31                                         | 2.68                                                                 | 3.24                                       |
| (CeSmZrTb)O <sub>2</sub>   | 2.06                                       | 3.21                                         | 2.52                                                                 | 2.18                                       |
| (LaSmZrTb)O <sub>2</sub>   | 2.14                                       | 3.32                                         | 1.85                                                                 | 2.15                                       |
| (LaPrZrTb)O <sub>2</sub>   | 1.96                                       | 3.1                                          | 3.32                                                                 | 2                                          |
| (SmPrZrTb)O <sub>2</sub>   | 1.99                                       | 3.32                                         | 2.93                                                                 | 2.02                                       |
| (CeYZrTb)O <sub>2</sub>    | 2.07                                       | 3.16                                         | 3.25                                                                 | 3.23                                       |
| (LaYZrTb)O <sub>2</sub>    | 2.22                                       | 3.23                                         | 3.17                                                                 | 2.3                                        |
| (SmYZrTb)O <sub>2</sub>    | 2.06                                       | 3.49                                         | 1.28                                                                 | 2.11                                       |
| (PrYZrTb)O <sub>2</sub>    | 2.03                                       | 3.43                                         | 2.85                                                                 | 2.02                                       |
| (CeLaSmPrY)O <sub>2</sub>  | 2.12                                       | 3.46                                         | 3.48                                                                 | 3.11                                       |
| (CeLaSmPrZr)O <sub>2</sub> | 1.97                                       | 2.74                                         | 2.65                                                                 | 2.08                                       |
| (CeLaSmYZr)O <sub>2</sub>  | 3.31                                       | 3.22                                         | 3.35                                                                 | 3.31                                       |
| (CeLaPrYZr)O <sub>2</sub>  | 2.02                                       | 3.31                                         | 2.62                                                                 | 2.05                                       |
| (CeSmPrYZr)O <sub>2</sub>  | 2.01                                       | 3.35                                         | 2.51                                                                 | 3.3                                        |
| (LaSmPrYZr)O <sub>2</sub>  | 2.09                                       | 3.09                                         | 2.89                                                                 | 2.16                                       |
| (CeLaSmPrTb)O <sub>2</sub> | 2.09                                       | 3.42                                         | 2.65                                                                 | 2.13                                       |
| (CeLaSmYTb)O <sub>2</sub>  | 2.22                                       | 3.5                                          | 3.5                                                                  | 2.32                                       |
| (CeLaPrYTb)O <sub>2</sub>  | 2.17                                       | 3.48                                         | 3.46                                                                 | 2.21                                       |
| (CeSmPrYTb)O <sub>2</sub>  | 2.14                                       | 3.41                                         | 2.66                                                                 | 2.19                                       |
| (LaSmPrYTb)O <sub>2</sub>  | 2.24                                       | 3.42                                         | 3.52                                                                 | 2.33                                       |
| (CeLaSmZrTb)O <sub>2</sub> | 2.14                                       | 3.38                                         | 2.73                                                                 | 2.14                                       |

| <b>Composition</b>             | <b>Band gap energy<br/>at 900 °C – air</b> | <b>Band gap energy<br/>at 900 °C – argon</b> | <b>Band gap energy<br/>at 900 °C – 10% H<sub>2</sub><br/>+ argon</b> | <b>Band gap energy<br/>at 900 °C – air</b> |
|--------------------------------|--------------------------------------------|----------------------------------------------|----------------------------------------------------------------------|--------------------------------------------|
| (CeLaPrZrTb)O <sub>2</sub>     | 2.02                                       | 2.51                                         | 2.6                                                                  | 2.15                                       |
| (CeSmPrZrTb)O <sub>2</sub>     | 2.04                                       | 2.46                                         | 2.58                                                                 | 2.12                                       |
| (LaSmPrZrTb)O <sub>2</sub>     | 2.02                                       | 3.38                                         | 3.3                                                                  | 2                                          |
| (CeLaYZrTb)O <sub>2</sub>      | 2.17                                       | 3.38                                         | 2.59                                                                 | 3.16                                       |
| (CeSmYZrTb)O <sub>2</sub>      | 2.17                                       | 3.37                                         | 2.61                                                                 | 3.21                                       |
| (LaSmYZrTb)O <sub>2</sub>      | 2.21                                       | 3.55                                         | 2.01                                                                 | 2.21                                       |
| (CePrYZrTb)O <sub>2</sub>      | 1.98                                       | 2.85                                         | 2.51                                                                 | 2.18                                       |
| (LaPrYZrTb)O <sub>2</sub>      | 2.07                                       | 3.37                                         | 2.58                                                                 | 2.24                                       |
| (SmPrYZrTb)O <sub>2</sub>      | 1.94                                       | 3.37                                         | 2.96                                                                 | 2.21                                       |
| (CeLaSmPrYZr)O <sub>2</sub>    | 2.08                                       | 3.36                                         | 3.37                                                                 | 2.09                                       |
| (CeLaSmPrYTb)O <sub>2</sub>    | 2.1                                        | 3.37                                         | 2.62                                                                 | 2.12                                       |
| (CeLaSmPrZrTb)O <sub>2</sub> 2 |                                            | 3.39                                         | 2.59                                                                 | 2.31                                       |
| (CeLaSmYZrTb)O <sub>2</sub>    | 2.15                                       | 3.31                                         | 2.63                                                                 | 2.24                                       |
| (CeLaPrYZrTb)O <sub>2</sub>    | 2.01                                       | 3.3                                          | 2.62                                                                 | 2.12                                       |
| (CeSmPrYZrTb)O <sub>2</sub>    | 1.96                                       | 3.37                                         | 2.59                                                                 | 2.56                                       |

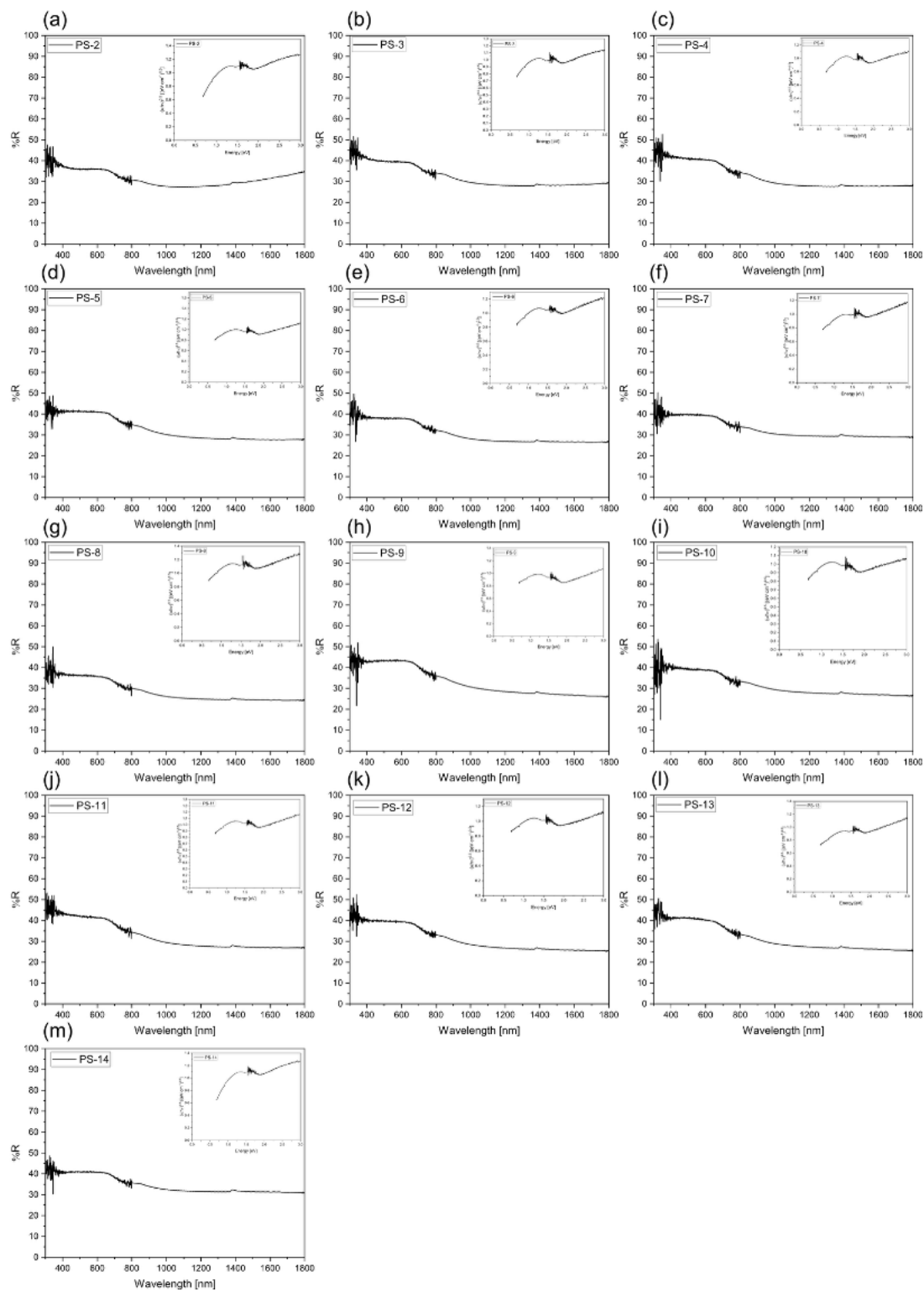


Figure 56: (a)-(m) The UV-Vis absorption spectra for samples PS-2 to PS-14 (Tauc plot for indirect transitions inset).

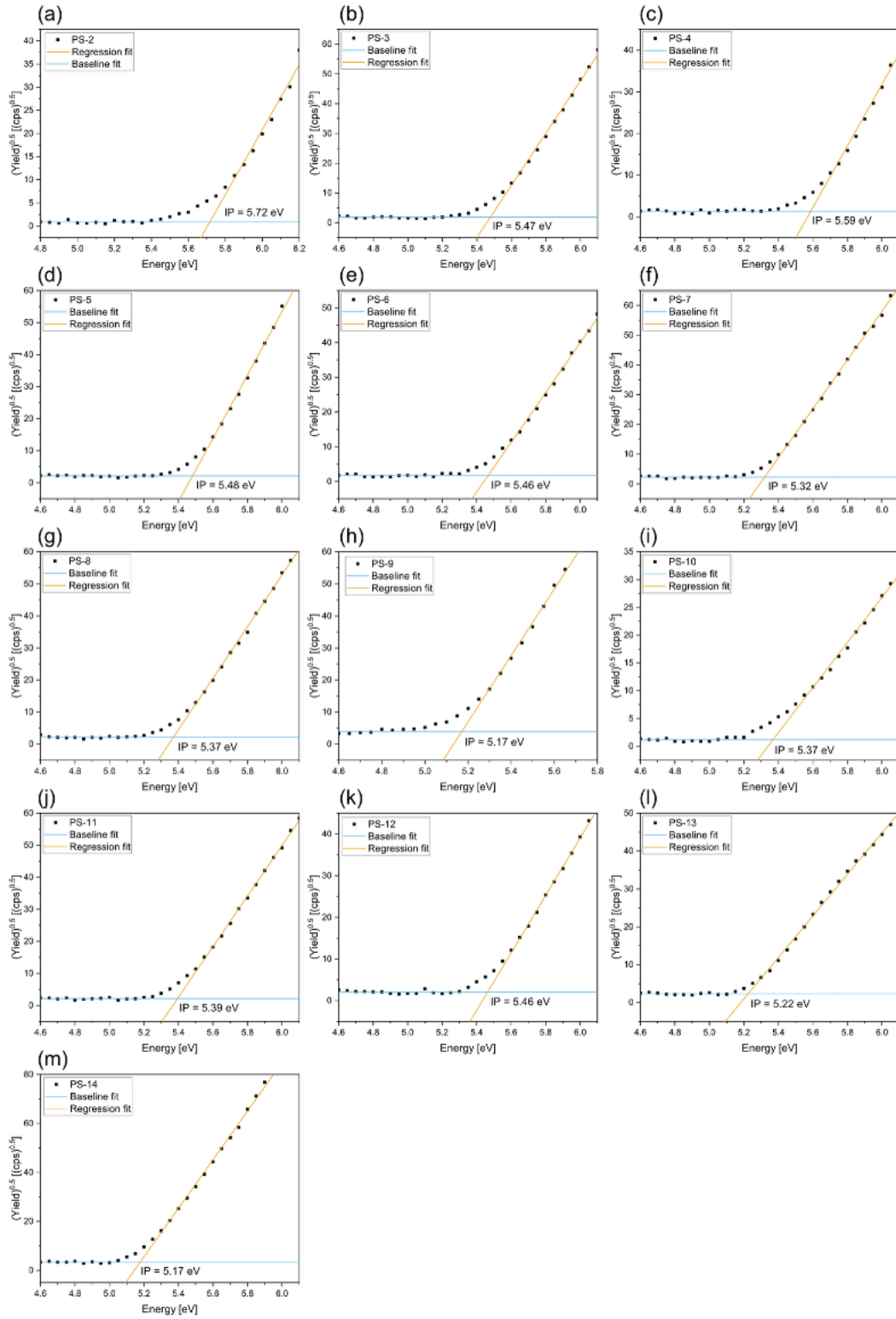


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## D List of Abbreviations

### Abbreviations

|               |                                                |
|---------------|------------------------------------------------|
| AFM           | Atomic force microscopy                        |
| ATR-IR        | Attenuated total reflectance-infrared          |
| BSE           | Back scattered electrons                       |
| CCC           | Charge carrier concentration                   |
| Cu-K $\alpha$ | X-ray source with copper K $\alpha$ radiation  |
| DFT           | Density functional theory                      |
| DRS           | Diffuse reflectance spectroscopy               |
| EDS           | Electron dispersive spectroscopy               |
| ETL           | Electron transport layer                       |
| FF            | Fill factor                                    |
| FIB           | Focused ion beam                               |
| Ga-K $\alpha$ | X-ray source with gallium K $\alpha$ radiation |
| HEA           | High-entropy alloy                             |
| HEI           | High-entropy iodide                            |
| HEM           | High-entropy material                          |
| HEO           | High-entropy oxide                             |
| HEPO          | High-entropy perovskite oxide                  |
| HOMO          | Highest occupied molecular orbital             |
| HTL           | Hole transport layer                           |
| IP            | Ionisation potential                           |
| JT            | Jahn-Teller                                    |
| JV            | Current density-voltage                        |
| LUMO          | Lowest unoccupied molecular orbital            |
| MPP           | Maximum power point                            |
| OER           | Oxygen evolution reaction                      |

## List of Abbreviations

|            |                                   |
|------------|-----------------------------------|
| PCE        | Power conversion efficiency       |
| PESA       | Photoelectron spectroscopy in air |
| PL         | Photoluminescence                 |
| PLD        | Pulsed laser deposition           |
| PSC        | Perovskite solar cell             |
| RCP        | Reverse co-precipitation          |
| RE         | Rare earth                        |
| RE-HEO     | Rare earth high-entropy oxide     |
| SE         | Secondary electrons               |
| SEM        | Scanning electron microscopy      |
| SOFC       | Solid oxide fuel cell             |
| TEM        | Transmission electron microscopy  |
| UV-Vis-NIR | Ultraviolet-visible-near infrared |
| VBM        | Valence band minimum              |
| XRD        | X-ray diffraction                 |
| XRF        | X-ray fluorescence                |

## Formula Symbols

|              |                                                     |
|--------------|-----------------------------------------------------|
| $E_g$        | Bandgap of material                                 |
| $J_{sc}$     | Short circuit current density                       |
| $n_A$        | Oxidation state of A-site in a perovskite structure |
| $R_\infty$   | Reflectance of an infinitely thick sample           |
| $r_A$        | A-site ionic radii in a perovskite structure        |
| $r_B$        | B-site ionic radii in a perovskite structure        |
| $r_X$        | X-site ionic radii in a perovskite structure        |
| $S_{config}$ | Configurational entropy                             |
| $V_{oc}$     | Open circuit voltage                                |

## List of Abbreviations

|                  |                                           |
|------------------|-------------------------------------------|
| $\mu_H$          | Hall mobility                             |
| $A$              | Absorbance of material                    |
| $C$              | Number of components                      |
| $d$              | Distance between lattice planes           |
| $E$              | Young's modulus                           |
| $F$              | Degrees of freedom                        |
| $h$              | Planck's constant                         |
| $H$              | Hardness                                  |
| $P$              | Maximum number of phases                  |
| $R$              | Universal gas constant                    |
| $T$              | Temperature                               |
| $t$              | Goldschmidt tolerance factor              |
| $\Delta G_{mix}$ | Gibbs free energy of formation            |
| $\Delta H_{mix}$ | Enthalpy of formation                     |
| $\Delta S_{mix}$ | Entropy of formation                      |
| $\theta$         | Angle of diffraction                      |
| $\lambda$        | Wavelength of incident radiation          |
| $\mu$            | Octahedral factor                         |
| $\nu$            | Frequency of incident radiation           |
| $\tau$           | Oxidation state-weighted tolerance factor |

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*I think I did pretty well, considering I started out with nothing but a bunch of blank paper.*

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