

## LETTER

# Synthesis and characterization of $\text{Ca}_{(1-x)}\text{Sm}_x\text{F}_{(2+x)}$ ( $0 \leq x \leq 0.15$ ) solid electrolytes for fluoride-ion batteries

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## Abstract

Calcium fluoride solid electrolytes have been identified as a candidate for solid-state fluoride-ion batteries (FIBs). Here, we investigate the doping of  $\text{CaF}_2$  with samarium —  $\text{Ca}_{1-x}\text{Sm}_x\text{F}_{2+x}$  ( $0 \leq x \leq 0.15$ ) — obtained by solid synthesis via high-energy ball milling. Structural, morphological, and ionic conductivity studies of the as-prepared materials were examined. It reveals that the fluorite-type structure is dominating with a crystallite size of 12–14 nm. The highest ionic conductivity at room temperature had been obtained for  $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{F}_{2.95}$  with a value of  $2.8 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ . It proves that a small content of Sm doping can considerably improve the ionic conductivity of  $\text{CaF}_2$ .

## KEYWORDS

Fluoride-ion battery, ionic conductivity, solid-state electrolytes

## 1 | INTRODUCTION

Calcium fluoride ( $\text{CaF}_2$ ) is a representative of the fluoride-type structured halides, an essential family of ionic materials with numerous applications also widely used in metallurgy, construction materials, optics, defense, and other industries.<sup>1,2</sup>  $\text{CaF}_2$  is a colorless or white crystalline powder and biocompatible material, which has a basic cubic fluorite-type structure.<sup>1,3,4</sup> The material is also well known for being a relative fast-ion conductor, a material in which the lighter ions ( $\text{F}^-$ ) acquire significant mobility comparable to ionic melts at temperatures well below its melting point, possibly useful for energy storage devices like supercapacitors and batteries.<sup>5,6</sup> All-solid-state batteries promising candidate and attention for a wide range of applications, including consumer electronics, automotive, renewable sources such as solar, and grid solutions. The developing of next-generation batteries has set all solid-state batteries into focus

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for which solid electrolytes (SEs) are a critical component for improved stability, safety, higher energy density compatibility, and utilization of cost-effective materials.<sup>7,8</sup>

Alternative approaches to Li-ion batteries (LIBs) like fluoride-ion batteries (FIBs) are theoretically even able to provide higher energy densities.<sup>9</sup> The chemistry of FIBs relies on the shuttle of fluoride ions ( $F^-$ ) between for instance metal and metal fluoride electrodes, through a fluoride ion-conducting SE.<sup>10</sup> Related studies have been focused on fluoride-ion conductors,<sup>10</sup> which still seemed to be a challenging issue at ambient temperatures when compared with liquid electrolyte performances.<sup>11</sup>

Two well-known fluoride classes of compounds with high ionic conductivity are of the fluorite-type (Fm-3m) and tysonite-type (P3c1) structures.<sup>12,13</sup> The fluorite-type structure is related to alkaline-earth fluorides ( $AEF_2$ :  $CaF_2$ ,  $BaF_2$ , and  $SrF_2$ ) and the tysonite-type structure to the rare-earth fluorides ( $REF_3$  with  $Re = La, Sm, Ce, Pr,$  and  $Nd$ ). In previous studies,  $La_{0.9}Ba_{0.1}F_{2.9}$  has been reported as a solid-state electrolyte that exhibits high ionic conductivities for FIBs applications at elevated temperatures.<sup>10</sup> Maximum ionic conductivities on single crystals were reported with La, Ce, Nd, and Sm doped with Ca, Ba, and Sr, vary from  $10^{-3}$  to  $10^{-5}$   $S\cdot cm^{-1}$  at room temperature (RT) and from  $10^{-2}$  to  $10^{-3}$   $S\cdot cm^{-1}$  at  $T = 150^\circ C$  or above.<sup>13,14</sup> In a previously reported investigation about a  $SmF_3$  synthesis, a conductivity jump for  $SmF_3$  was found around  $500^\circ C$ , which corresponds to the orthorhombic ( $YF_3$ )-trigonal ( $LaF_3$ ) phase providing an elevated ionic mobility for the tysonite-type network.<sup>15</sup> Recently, we reported that nano-powdered  $Sm_{0.95}Ca_{0.05}F_{2.95}$  material exhibits an ionic conductivity around  $10^{-5}$   $S\cdot cm^{-1}$  at RT.<sup>16,17</sup>

Here, we investigated the unique behavior of fluoride ion-based-conducting SEs with  $SmF_3$ -doped  $CaF_2$  and prepared  $Ca_{1-x}Sm_xF_{2+x}$  ( $0 \leq x \leq 0.15$ ) solid solutions by applying high-energy ball milling without material preprocessing or post-processing.

## 2 | MATERIALS AND METHODS

Solid-state synthesis (high-energy ball milling) was used to prepare samarium-substituted calcium fluoride materials. The precursor materials ( $CaF_2$ , 99%, and  $SmF_3$  anhydrous, 99.9%, REO) were obtained from Alfa Aesar. The stoichiometric compositions of  $Ca_{1-x}Sm_xF_{2+x}$  ( $0 \leq x \leq 0.15$ ) were synthesized by high-energy planetary ball milling. The as-prepared materials' preparation was similar to authors' previous reports.<sup>16,18</sup>

The structural and morphological studies of as-prepared materials were carried out by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD measurements were conducted via an AXS Bruker D5005 Advanced instrument with Cu  $K\alpha$  radiation ( $\lambda_1 = 1.54056 \text{ \AA}$ ;  $\lambda_2 = 1.544390 \text{ \AA}$ ). SEM investigations of the ball-milled electrolytes' microstructures were performed with 4-kV electron high tension (EHT) applying a width of 4 mm.

Electrochemical impedance spectroscopy (EIS) measurements were carried out on solid-state electrolyte pellets assembled with a pellet press. The pellets were sputtered with gold coating on both sides to block ions from the electrodes. The thickness and diameter of the pellets were approximately 1 and 10 mm, respectively. The impedance measurements were conducted with an Agilent 4192A LF impedance analyzer over a frequency range from 5 Hz to 13 MHz at a voltage amplitude of 10 mV, with spectra recording at RT.<sup>19</sup>

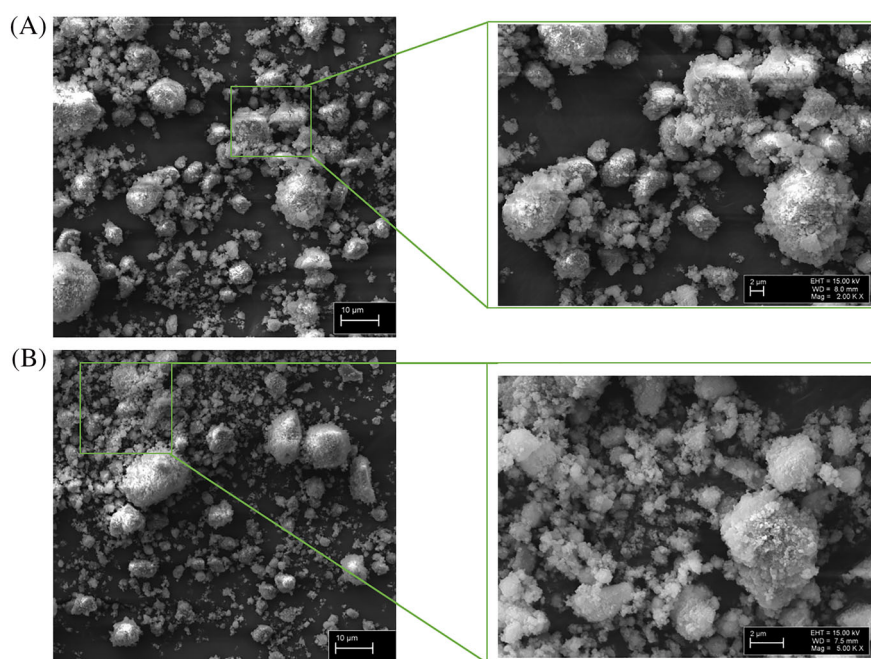
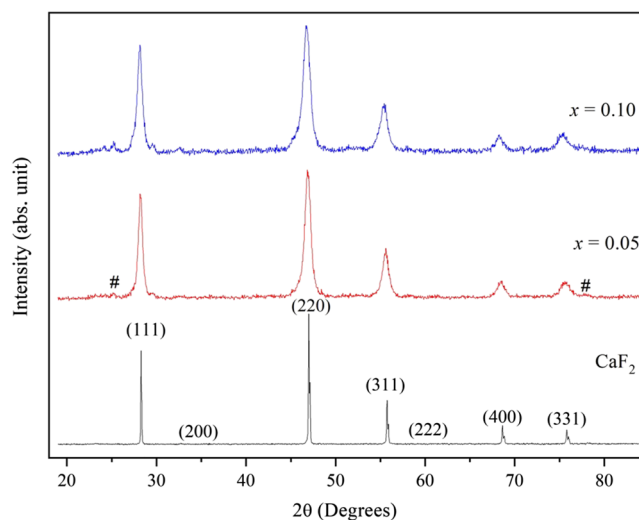
## 3 | RESULTS AND DISCUSSION

### 3.1 | Structural and morphological studies

Continuing previous studies, we synthesized and investigated the reverse doped material:  $Ca_{1-x}Sm_xF_{2+x}$  ( $0 \leq x \leq 0.15$ ) solid-state fluoride conductor. The as-prepared samples exhibit a fluorite-type cubic structure revealed by XRD patterns of  $Ca_{0.95}Sm_{0.05}F_{2.95}$  ( $a = 5.4837 \text{ \AA}$  with space group Fm-3m) (see Figure 1). As per synthesis, we found minor diffraction peaks from the  $YF_3$ -type orthorhombic structure originating from  $SmF_3$ . For this sample, the crystallite size was estimated with the Scherrer equation around 12–14 nm. Slight changes in unit cell dimensions, particle size/shape, agglomeration/packing, created defects, and geometry frustrations at grain boundaries within the ball-milled powder are considered.<sup>19–21</sup>

The SEM microstructures of as-prepared materials' studies were carried out and is illustrated in Figure 2A,B. The electrolyte samples provided particle sizes of 50–70 nm. A minor content of agglomerates of  $CaF_2$  sizes ranging from a

**FIGURE 1** XRD patterns of  $\text{Ca}_{1-x}\text{Sm}_x\text{F}_{2+x}$  ( $x = 0.05$  and  $0.10$ ) are given: pure  $\text{CaF}_2$  (black color), ball-milled electrolyte (red and blue color), while “#” symbol represents minor  $\text{SmF}_3$  orthorhombic phase contributions

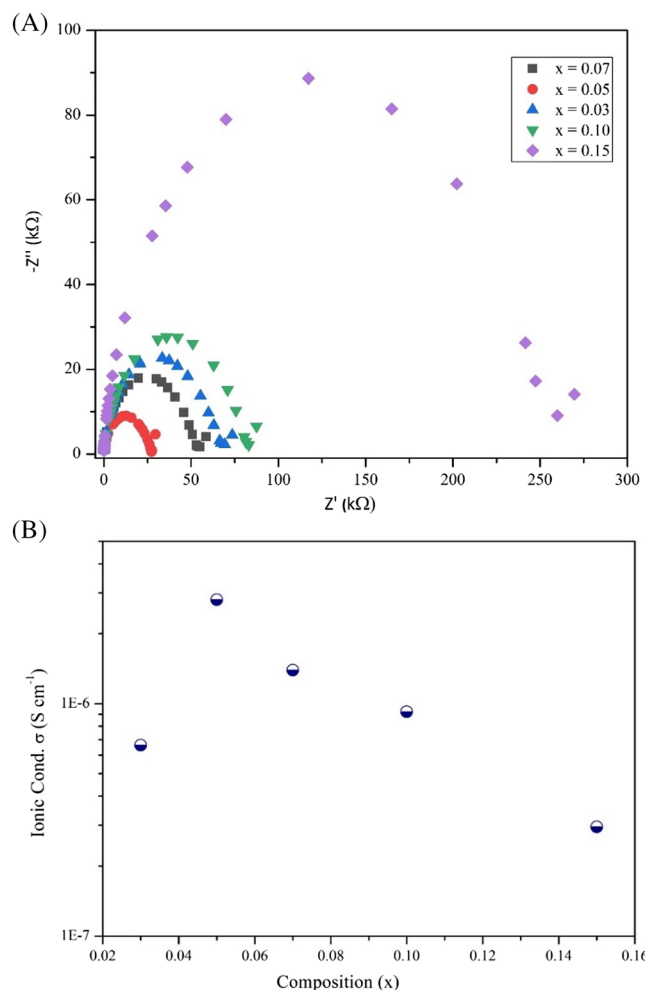


**FIGURE 2** SEM images of (A)  $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{F}_{2.95}$  and (B)  $\text{Ca}_{0.90}\text{Sm}_{0.10}\text{F}_{2.90}$  with different magnifications. The as-prepared samples are agglomerated, and pristine particles can be observed

few dozens to several tens of nanometers is typically being observed. The synthesized samples are pristine and agglomerated during the milling.

### 3.2 | EIS investigations

EIS studies were applied to determine the ionic conductivities. The Nyquist plots of the as-prepared  $\text{Ca}_{1-x}\text{Sm}_x\text{F}_{2+x}$  ( $0 \leq x \leq 0.15$ ) samples are presented in Figure 3A. The spectra consist of two region parts: a semicircle at high frequencies (MHz)—related to the ionic conductivity with grain boundaries — and a straight line towards low frequencies (Hz) — referring to the electrolyte–electrode polarizing interface phenomenon.<sup>22</sup> The fluoride ionic conductivity was determined by the equation  $\sigma = [t/(R \times A)]$  (with resistance  $R$ , thickness  $t$ , and pellet surface  $A$ ).<sup>16</sup> Different stoichiometric levels of  $\text{Ca}_{1-x}\text{Sm}_x\text{F}_{2+x}$  ( $x = 0.03, 0.05, 0.07, 0.10,$  and  $0.15$ ) solid electrolytes for their ionic conductivities were measured at room temperature in the range of  $10^{-6}$  to  $10^{-7} \text{ S}\cdot\text{cm}^{-1}$  at RT were achieved (see Figure 3B). The maximum value at RT was obtained for  $x = 0.05$  with  $2.8 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ . This is roughly one magnitude higher than of



**FIGURE 3** In (A), the Nyquist plots of  $\text{Ca}_{1-x}\text{Sm}_x\text{F}_{2+x}$  ( $x = 0.03, 0.05, 0.07, 0.10,$  and  $0.15$ ) electrolytes at RT are depicted. The RT ionic conductivities versus as-prepared materials' composition (maximum for  $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{F}_{2.95}$  with  $2.8 \times 10^{-6}$  S·cm<sup>-1</sup>) are presented in (B)

**TABLE 1** Summary of  $\text{CaF}_2$ - and  $\text{SmF}_3$ -based fluoride-ion conductors of various synthesis approaches

Solid electrolyte	Ionic conductivity: $\sigma$ (S·cm <sup>-1</sup> )	Methods and reference
$\text{Sm}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$	$1.0 \times 10^{-4}$ (RT)	High temperature-driven solid-state synthesis + mixing (Dieudonné et al. <sup>15</sup> )
h- $\text{CaF}_2$	$1.9 \times 10^{-5}$ (RT)	Vapor pressure exposure + ball milling (Molaiyan and Witter <sup>18</sup> )
$\text{Sm}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$	$2.8 \times 10^{-5}$ (RT)	High-energy ball milling (Molaiyan and Witter <sup>16</sup> )
$\text{SmF}_3$ (single crystal)	$5.0 \times 10^{-4}$ (550°C)	Melting method (Karimov et al. <sup>24</sup> )
$\text{SmF}_3$ (BM)	$1.1 \times 10^{-6}$ (RT)	High-energy ball milling (Molaiyan and Witter <sup>16</sup> )
$\text{Ca}_{0.95}\text{Sm}_{0.05}\text{F}_{2.95}$	$2.8 \times 10^{-6}$ (RT)	High-energy ball milling (this work)
$\text{CaF}_2$ (BM)	$1.9 \times 10^{-7}$ (RT)	High-energy ball milling (Molaiyan and Witter <sup>18</sup> )
$\text{CaF}_2$ (single crystal)	$8 \times 10^{-8}$ (260°C)	Single-crystal melting method (Ravi et al. <sup>25</sup> )

Abbreviation: RT, room temperature.

pure ball-milled  $\text{CaF}_2$  ( $1.98 \times 10^{-7}$  S·cm<sup>-1</sup>) but lower than best results obtained for the reverse doping:  $\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}$  ( $x = 0.05: 2.8 \times 10^{-5}$  S·cm<sup>-1</sup>).<sup>15,23</sup>

There are numerous reports on enhancing the ionic conductivity of nanocrystalline materials like  $\text{CaF}_2$ , and other dopant compounds,<sup>13</sup> the exact mechanism of conduction, defect chemistry, and the disorder's nature has a variety of reasons. Related different synthesized and investigated classes of SEs are compiled for comparison in Table 1.

In a previous report, it had been indicated that calcium fluoride ionic conductivity was increased by two orders of magnitude, to  $1.9 \times 10^{-5}$  S·cm<sup>-1</sup> at RT, with enhanced surface defect structure, due to the application of vapor pressure exposure followed by high-energy ball milling.<sup>18</sup> Alternatively, a  $\text{CaF}_2$  doping of  $\text{SmF}_3$  ( $\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}$ ) within the

stoichiometric ratio range  $0 \leq x \leq 0.15$  significantly increased the ionic conductivity of  $\text{Sm}_{0.95}\text{Ca}_{0.05}\text{F}_{2.95}$  ( $2.8 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ ) at RT. Recently, Karimov et al.<sup>24</sup> reported that tysonite  $\text{SmF}_3$ -based ( $\text{LaF}_3$ -type) phases of  $\text{Sm}_{1-y}\text{M}_y\text{F}_{3-y}$  fluoride ion-conducting SEs substituting  $\text{Sm}^{3+}$  with  $\text{M}^{2+}$  ( $M = \text{Ca}, \text{Sr}, \text{or Ba}$ ) or vice versa provide maximum values of  $5 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$  at  $550^\circ\text{C}$  (for  $y = 0.05$ ). This supports our finding that  $\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}$  materials provide higher ionic conductivities than to reverse doped compounds.

## 4 | CONCLUSIONS

$\text{Ca}_{1-x}\text{Sm}_x\text{F}_{2+x}$  ( $0 \leq x \leq 0.15$ ) solid-state electrolytes were successfully prepared by solid synthesis (high-energy ball milling), a basic and scalable nano-powder preparation method. Structural and morphological studies reveal that the materials possess the fluorite-type structure with crystallite sizes around 12–14 nm and particle sizes of 50–70 nm. RT fluoride ionic conductivities were obtained to be in the range of  $10^{-6}$  to  $10^{-7} \text{ S}\cdot\text{cm}^{-1}$  with the maximum of  $2.8 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$  for  $\text{Ca}_{0.95}\text{Sm}_{0.05}\text{F}_{2.95}$  motivating further improvements and investigations. Future studies would recommend a posttreatment removing contamination and accommodating surface defect enhancements along a systematic hand-in-hand structural and morphological analysis with continuous parameter variations of chemical composition for improving its electrochemical applicability.

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## CONFLICT OF INTERESTS

There is no conflict of interest.

## DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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