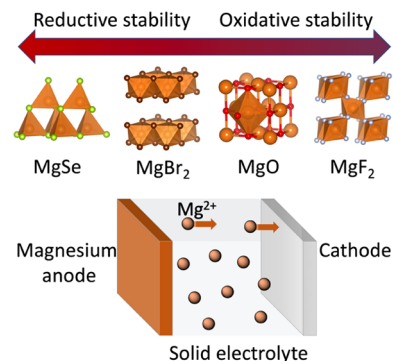


Stability of Magnesium Binary and Ternary Compounds for Batteries Determined from First Principles

Mohsen Sotoudeh* and Axel Groß*

ABSTRACT: Electrochemical stability is a critical performance parameter for the materials used as electrolytes and electrodes in batteries. Using first-principles electronic structure calculations, we have determined the electrochemical stability windows of magnesium binary and ternary spinel compounds. These materials are candidates for protective coatings, solid electrolytes, and cathodes in Mg batteries, which represent a promising sustainable alternative to Li-ion batteries that still dominate the battery market. Furthermore, we have applied and assessed two different criteria for the chemical stability of the compounds. For the spinel materials, we identify the critical role of the ionic radii of the transition metal for the stability of the compounds. In addition, we determine the ion mobility in these materials using a recently developed descriptor. We thus provide guidelines for the choice of promising solid materials for Mg batteries with improved properties.



Due to the importance of electrochemical energy storage devices for our future sustainable energy technology, there is a continuing quest for batteries with improved properties. In the last decades, lithium-ion batteries (LIBs) have dominated the battery market, but it appears that the increase of the performance of LIBs is now facing physicochemical limits.¹ In order to overcome these limitations, either new advanced Li-ion technologies can be developed² or alternative battery technologies that do not rely on Li, so-called post-Li-ion batteries,^{3,4} can be employed. The post-Li-ion strategies switch to different mobile cations such as Na^+ ⁴⁻⁷ or Mg^{2+} ,⁸⁻¹¹ which benefit from the high natural abundance of these elements to lower the battery cost compared to lithium-ion batteries. Furthermore, Mg batteries can be safely operated with an Mg metal anode leading to considerable improvements in energy densities^{12,13} without being plagued by dendrite growth in the same way as lithium metal anodes do.¹⁴⁻¹⁸ Among them, batteries based on the bivalent magnesium cation achieve higher volumetric energy densities compared to monovalent-based batteries.^{12,13} However, this bivalent nature also leads to a stronger interaction with host lattices and solvents which limits the ionic conductivity.¹⁹ Furthermore, decomposition of electrolytes on Mg electrodes,²⁰ forming passivation layers, reduces the battery performance. However, not only electrolytes but also electrode materials can degrade when exposed to bivalent charge carriers. Hence, the stability of battery materials is a critical parameter decisive for the performance and lifetime of batteries under operating conditions. This is, for example, reflected in the fact that in LIBs, in general, flammable electrolytes are still used, in spite of the hazards associated with such electrolytes,¹⁸ simply due to the fact that there are still

no effective and inexpensive alternative electrolytes available that are stable over the large potential range of more than 4 V required for LIBs.

In this computational study, we address the stability of magnesium binary and ternary compounds for batteries using first-principles periodic electronic structure calculations based on density functional theory. Mg binaries are simple compounds that can be used as coating materials for Mg metal anodes in order to prohibit electrolyte degradation. In particular, Mg halides have been identified as suitable coating materials due to a favorable electrochemical stability together with a suitable Mg ion mobility.^{21,22} On the other hand, Mg ternary materials such as inorganic oxides,^{23,24} hydrides,²⁵⁻²⁷ and chalcogenides²⁸⁻³⁰ exhibit good bulk Mg ionic conductivities. Among them, chalcogenide spinel lattices were identified as Mg-ion conductors with a high ion mobility^{28,30} which is a critical property for both electrodes and solid electrolytes. Spinel compounds including transition metals such as Cr and Mn have high Mg binding energies³¹ together with a satisfactory electron conductivity which makes them suitable as cathode materials. On the other hand, closed-shell systems such as Sc and Y have a rather low electron conductivity which is a prerequisite for their usage as solid electrolytes.^{28,32}

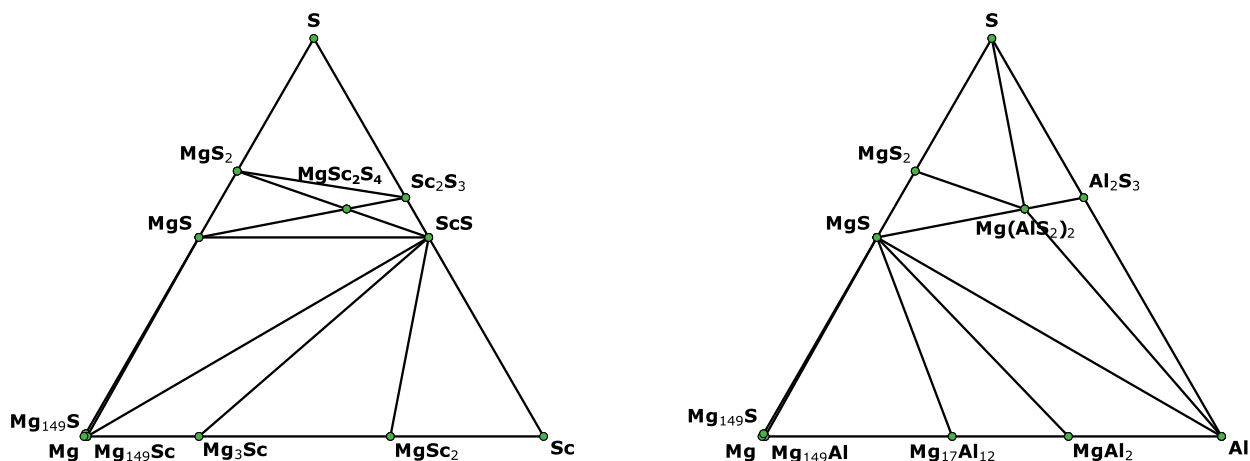


Figure 1. Ternary phase diagrams for the Mg–Sc–S and Mg–Al–S systems. The labels and points correspond to the stable crystalline phases calculated by the energy above the hull. The lines underline the reaction vectors with respect to the different elemental concentrations for the stable phases.

To be specific, we have determined the electrochemical stability window for a series of Mg binary and ternary compounds. Recently, we have developed a descriptor, the migration number, for the ion mobility that is based on the ionic radii, the oxidation states, and the difference in the Pauling electronegativities of the involved species.³³ These physical factors describe the height of the migration barriers of a series of binary, ternary, and quaternary phases through linear scaling relations. Here we will, in particular, focus on the fact whether the parameters entering the migration number are also decisive factors for the stability of the corresponding compounds. As far as the Mg binaries are concerned, we will particularly focus on the electronegativity and link it to the band gap of the considered materials.

With regard to the Mg ternaries, we concentrate on Mg sulfide spinels because of their favorable ion mobility properties.^{28,32,33} We will vary the transition metals of these compounds and particularly focus on the role of the ionic radius of the transition metal cation on the stability of the spinels. Again we will discuss the correlation between the stability and ion mobility of these compounds. Thus, we link two parameters that are critical for the performance of Mg batteries and provide guidelines for the identification of promising alternative materials with improved properties.

■ COMPUTATIONAL DETAILS

DFT Calculations. First-principles calculations have been performed in the framework of density functional theory (DFT)^{34,35} addressing the properties of binary Mg_nX_m and ternary MgB_2S_4 spinel compounds. The exchange-correlation effects were described by the generalized gradient approximation (GGA) functional PBE³⁶ and the hybrid functional HSE06³⁷ with a typical mixing factor of 0.2.

We have used the Vienna *Ab-Initio* Simulation Package^{38–40} together with the projector augmented wave (PAW)^{40,41} method. The electronic structure was converged to 1×10^{-5} eV, applying a plane wave cutoff of 520 eV. A $4 \times 4 \times 4$ k-point mesh has been used for the unit cells of the Mg_nX_m binaries. The ternary MgB_2S_4 spinel calculations were optimized using $2 \times 2 \times 2$ k-point meshes for the unit cell containing eight formula units. The partial occupancies are set for each orbital using the tetrahedron method^{42,43} and the so-called Blöchl corrections.⁴⁴ All atomic positions are optimized without symmetry

constraints to obtain the ground state configurations. The initial configurations are taken from the Materials Project (MP) database.⁴⁵ We used the $Fd\bar{3}m$ space group for the MgB_2S_4 spinels, corresponding to a face-centered cubic structure. The Mg binaries ground state structures, as taken from the MP database, correspond to different space groups, as listed below.

In order to determine the Mg-ion migration barriers for the single-ion migration path between two tetrahedral sites passing the octahedral site, the nudged elastic band (NEB)^{46,47} method with the climbing image modification⁴⁸ has been applied in the low-vacancy limit. In detail, we removed just one migrating cation within the supercell, for example resulting in a $Mg_{0.875}B_2S_4$ stoichiometry of the spinel compounds. In all binary and ternary compounds, a sufficiently large supercell has been chosen for the NEB calculations to ensure a negligible interaction between the periodic images of the migrating ions. All structures were fully relaxed until the forces on the atoms were converged within $0.05 \text{ eV } \text{Å}^{-1}$.

The NEB calculations have been carried out with seven distinct images for the binary compounds and four distinct images between the tetrahedral and octahedral sites for the ternary spinels to evaluate the Mg-ion migration minimum energy path. Note that the diffusion in the considered compounds corresponds to interstitial diffusion. The calculations for the ternary compounds were carried out in a charge-neutral fashion, whereas for the binaries a compensating background charge was applied in the NEB calculations, as in these materials typically the overall charge neutrality is ensured by an equal amount of anion and cation vacancies.

Stability Window. The electrochemical stability window is commonly used to indicate the potential range in which the substance is neither oxidized nor reduced. Out of this range, the substance will react and decompose. We examine the implications of exposing the solid electrolytes to these high magnesium potentials without permitting any additional reaction between the electrolyte and the anode or cathode materials. The stability window is determined by the voltages at which magnesium is extracted from the electrolyte, forming an Mg-deficient decomposition layer between the solid electrolyte and the cathode, and when magnesium is inserted into the electrolyte, forming the Mg-reduced decomposition layer.

In the Mg binaries, below 0 V vs Mg/Mg^{2+} , metallic Mg is the stable form. Above 0 V, the binaries consisting of oxidized Mg

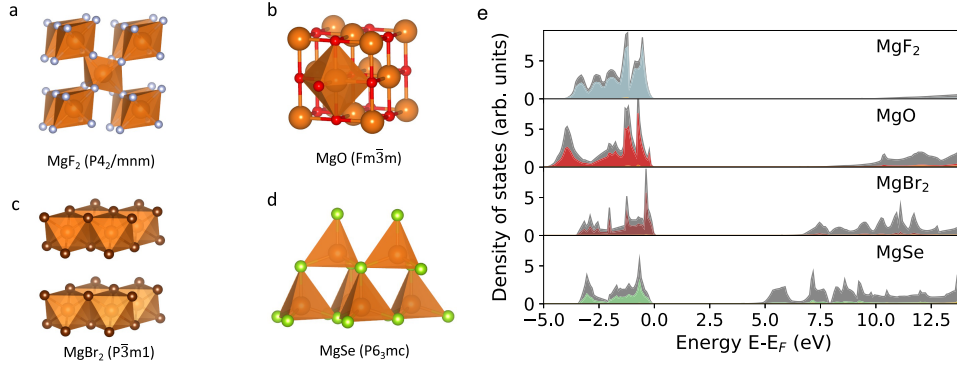


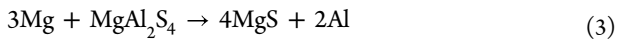
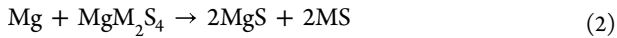
Figure 2. Structures of (a) MnF_2 , (b) MgO , (c) MgBr_2 , and (d) MgSe . Mg is colored orange, O red, F light blue, Br brown, and Se light green. The corresponding space groups of the binaries are provided in parentheses. The right graph (e) shows the calculated density of states (DOS) using the hybrid functional HSE06. The total DOS is given in black, and the projected DOS is shown in light blue for F- p , red for O- p , brown for Br- p , and light green for the Se- p orbitals, respectively.

together with the anions are stable up to a voltage that corresponds to the formation energy ΔG_f^0 , of the binaries,

$$\Delta V = -(\Delta G_f^0/zF) \quad (1)$$

where F is the Faraday constant and z corresponds to the elementary charges that are transferred upon the discharging reaction with $z = 2$ for Mg batteries. At higher voltages, magnesium is extracted, providing the oxidized cations.

Ternary Mg–M–S phase diagrams are constructed for each spinel compound utilizing a library of DFT computed bulk energies of materials with crystal structures from the Materials Project database,⁴⁵ as shown in Figure 1. The stability of ternary systems containing Mg, a second metal M, and sulfur will be briefly reviewed to demonstrate the principles and methodology involved. For the sake of simplicity, assume that only two binary sulfides of M, nominally MS and M_2S_3 (for Al, there is only Al_2S_3), are stable, that no phases exist between Mg and M, and that only one ternary phase exists, MgM_2S_4 . The thermodynamic parameters of the triangle MgM_2S_4 – MgS –MS (for Al, MgAl_2S_4 – MgS –Al) in Figure 1 will determine its limits of stability in the low-potential magnesium-rich direction, and those in the triangle MgM_2S_4 – M_2S_3 –MS (for Al, MgAl_2S_4 – Al_2S_3 –Al) will determine its limit of stability in the high-potential magnesium-poor direction, in the case of the possible solid electrolyte phase MgM_2S_4 . Therefore, for these ternary spinels, the lower limit of the stability window has been obtained using the relevant Mg decomposition reaction between the solid electrolyte and the anode



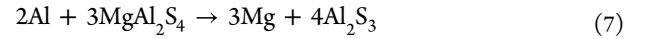
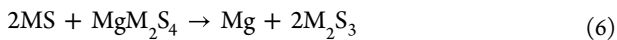
and the minimum voltage vs magnesium is determined from

$$V = -(\Delta G_r^0/zF) \quad (4)$$

where

$$\Delta G_r^0 = \Delta G_f^0(\text{products}) - \Delta G_f^0(\text{reactants}) \quad (5)$$

Likewise, the maximum potential up to which this phase remains stable is determined by the Mg spinel decomposition reaction involving the solid electrolyte and the cathode



This can be converted to a voltage vs magnesium by using eqs 4 and 5. Note that we determined the stabilities of all considered solid electrolytes for a temperature of 0 K.

The Mg binaries are the simplest ionic compounds that contain just the bivalent cation Mg^{2+} and one type of anion X^{n-} in various ratios depending on n . Different structures may exist for each composition depending on the relative sizes of the anions. We considered compositions with the commonly found stoichiometries in theoretical ground state configurations reported in the Materials Project (MP) database.⁴⁵ The local environment of the Mg-ion in the binary structures has been sketched in Figure 2 for magnesium fluoride, oxide, bromide, and selenide together with the density of states (DOS) of the compounds. Whereas the PBE functional yields a good description of the minimum energy structures and the relative energies of the Mg binaries, it typically underestimates the band gap of semiconductors and insulators.⁴⁷ Therefore, the HSE06 hybrid functional has been used to get reliable band gaps. Note that a very low electronic conductivity is a prerequisite that a crystalline material can be used as a solid electrolyte¹ but also as a protective coating. In fact, a simple relation between band gap and electronic conductivities does not exist theoretically, and the charge carrier density and mobility can describe electronic conductivity. The charge carrier density in band gap materials can be controlled by, for example, defect densities as a function of temperature and doping,⁴⁹ while mobility also depends on electron–phonon coupling. Still, in our study we discuss the properties of single crystals without considering defects, and for such materials the population of the conduction band is controlled by the Boltzmann factor where the band gap plays the crucial role.

The stable rutile structure of MgF_2 (Figure 2a) reflects the strong tendency of Mg^{2+} to acquire an octahedral coordination. Each Mg atom is coordinated to six F atoms which connect to three Mg anions. The calculated HSE06 band gap for MgF_2 of 10.37 eV is consistent with the experimental value of 10.8 eV,⁵⁰ the largest for all Mg binary structures considered here. For this compound, the filled valence band is dominantly of F- p character (light blue) which extends from -4 to 0 eV. The rock-salt structure of MgO (Figure 2b) is the structure in which the cations occupy all octahedral sites in a cubic close packed array of anions. Both anions and cations are 6-fold coordinated; an octahedron of six counterions surrounds each ion. The

calculated band gap of 7.71 eV is in good agreement with the experimental result of 7.77 eV.⁵¹ The filled valence band of MgO is of dominantly O-*p* character (red), extending from -5 to 0 eV. The MgBr₂ compound (Figure 2c) shows a layered structure in which the close-packed layers are bonded via weak van der Waals interactions between the bromine atoms of the adjacent layers. Each Mg cation is surrounded by six Br anions. The calculated band gap of this compound is 6.44 eV. The filled valence band of MgBr₂ consists mainly of Br-*p* states (brown) extending from -3.5 to 0 eV. In the wurtzite structure of MgSe (Figure 2d), the Mg cations occupy half the tetrahedral sites. In this structure, both cations and anions are 4-fold coordinated. The local symmetries of the cations and anions are identical with respect to their nearest neighbors but differ at the second-nearest neighbor distances. This compound exhibits a band gap of 4.67 eV. Like other Mg binary compounds, the valence band is dominated by *p* orbitals (light green) of the anion.

The band gaps of all considered Mg binaries calculated with the HSE functional together with their ground state space groups are listed in Table 1, and they agree well with previously

Table 1. Space Groups of the Considered Mg Binary Compounds Together with Their Band Gaps in eV Calculated with the HSE06 Hybrid Functional

System	Space group	Band gap
MgH ₂	<i>P4</i> ₂ / <i>mnm</i>	5.44
MgB ₂	<i>P6</i> / <i>mmm</i>	0.00
Mg ₂ Si	<i>Fm</i> $\bar{3}$ <i>m</i>	0.92
Mg ₂ Ge	<i>Fm</i> $\bar{3}$ <i>m</i>	0.85
Mg ₃ N ₂	<i>Ia</i> $\bar{3}$	3.01
Mg ₃ P ₂	<i>Ia</i> $\bar{3}$	2.32
Mg ₃ As ₂	<i>Ia</i> $\bar{3}$	2.14
MgO	<i>Fm</i> $\bar{3}$ <i>m</i>	7.71
MgS	<i>Fm</i> $\bar{3}$ <i>m</i>	4.26
MgSe	<i>P6</i> ₃ <i>mc</i>	4.67
MgTe	<i>P6</i> ₃ <i>mc</i>	3.92
MgF ₂	<i>P4</i> ₂ / <i>mnm</i>	10.37
MgCl ₂	<i>R</i> $\bar{3}$ <i>m</i>	7.61
MgBr ₂	<i>P</i> $\bar{3}$ <i>m</i> 1	6.44
MgI ₂	<i>P</i> $\bar{3}$ <i>m</i> 1	4.79

reported computations.²² Magnesium diboride MgB₂ has no band gap, whereas magnesium silicide (Mg₂Si) and germanide (Mg₂Ge) exhibit small band gaps below 1 eV. The remaining

compounds show a broad range of band gaps of up to 10.37 eV for MgF₂. Most of them have band gaps higher than 3 eV, which effectively make them insulators, whereas magnesium phosphide (Mg₃P₂) and arsenide (Mg₃As₂) have band gaps slightly above 2 eV.

In order to understand the origin of the wide range of band gaps observed in the Mg binaries, we have plotted the band gaps as a function of the Pauling electronegativity of the Mg binding partners in the binaries in Figure 3a. We find a strong correlation between electronegativity and band gaps, reflected in an approximate linear scaling between these two properties. Strongly electronegative anions such as F indicative of strong ionic bonding characteristics lead to a wide band gap, whereas weakly electronegative anions such as B with metallic bonding characteristics show small or vanishing band gaps.

The electrochemical stability windows of the binary compounds vs Mg/Mg²⁺ calculated according to eq 1 are plotted in Figure 4. For binaries, Mg-triols and Mg-tetrels exhibit poor stability reflected in the small stability window and consequently low oxidation resistance. Mg-pnictogens are associated with a larger stability window. For example, Mg₃N₂ will be stable over a range from 0 to 0.75 V at room temperature. However, the widths of the stability windows are still rather small (<1.0 V). In contrast, all of the Mg-halogens and Mg-chalcogens are notably more stable over a broader range of potentials at room temperature. Interestingly, the oxidative stabilities exhibit a strong correlation with the anion electronegativities. For a strongly electronegative anion such as F, the corresponding binary MgF₂ compound is stable against Mg up to potentials of more than 5 V. Consequently, among all considered binaries, Mg chalcogenides and halides exhibit the highest stability. A similar attempt based on the grand potential approach has been made in a recent computational study of binary materials in Mg batteries.²¹ It has been shown that oxidative stability correlates with anion electronegativity for Mg binary compounds, and a similar trend has been found in this recent computational study for coating materials.

A further critical parameter for solid state electrolytes is their ionic conductivity. From a crystallographic perspective, ionic crystals such as Mg binaries are characterized by two sublattices, namely a cationic sublattice and an anionic sublattice. Typically, the diffusion of ions is restricted to their corresponding sublattice. Thus, the Mg²⁺ diffusion mechanism is restricted to the cationic sublattices; diffusion mechanisms correlated with the anion sublattice (interstitialcy) usually do not occur. In such

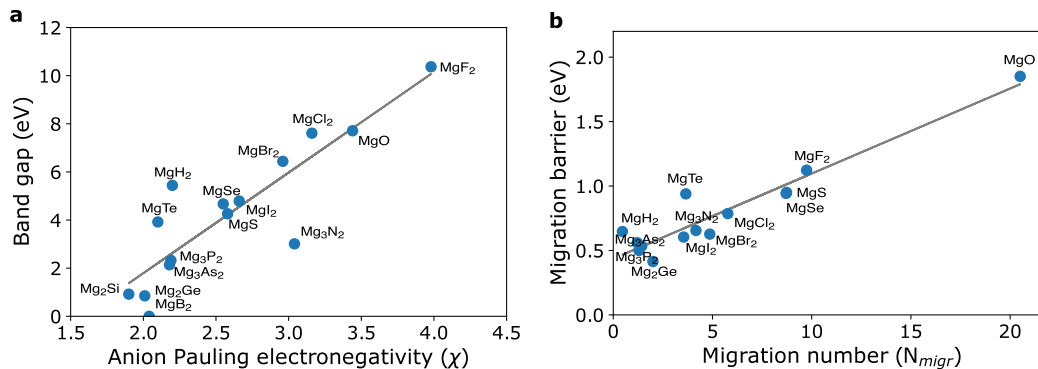


Figure 3. Electronegativity effects on the band gaps and migration barriers of Mg binaries. (a) Calculated band gap of Mg binaries using the hybrid functional HSE06 as a function of the anion electronegativity (χ). The gray line is a linear regression of these results. (b) Migration barriers of Mg binaries, derived from periodic DFT-PBE calculations combined with the NEB method, as a function of the migration number (N_{migr}).

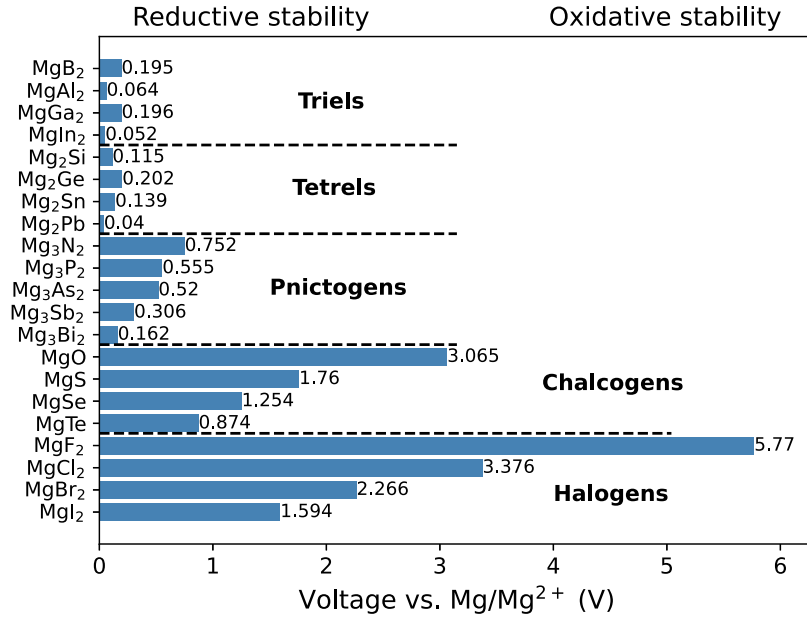


Figure 4. Electrochemical stability windows of Mg binaries indicating the voltages vs Mg metal at which the binaries are stable and not decomposed. Compounds are listed through the anions group in the periodic table.

ionic crystals, diffusion and ionic conduction require the presence of mobile point defects. Note that usually the defect concentration is small in the pure ionic crystals, even close to the melting temperature. For example, ionic crystals such as MgO or NaCl show low ionic conductivities even at high temperatures, caused by the small point defect concentration.

In alkali halides, Schottky disorder, in which both cation vacancies (V_C) and anion vacancies (V_A) create vacancy defect pairs, is dominant. In undoped crystals with Schottky disorder, equal site fractions of cation and anion vacancies are required for charge neutrality reasons. In thermal equilibrium, the product of the vacancy concentrations for the cations, C_{V_C} , and for the anions, C_{V_A} , is temperature-dependent according to

$$C_{V_C} C_{V_A} = \exp\left(-\frac{G_{SP}}{k_B T}\right) = K_{SP}(T) \quad (8)$$

where G_{SP} is the Gibbs free energy for the Schottky pair formation and $K_{SP}(T)$ denotes the Schottky product. In order to ensure an equal amount of anion and cation vacancies in our migration barrier simulations, a compensating background charge was applied in the NEB calculations for the binary compounds using the PBE functional.

Recently, we proposed a descriptor for the ion mobility, the so-called migration number:³³

$$N_{migr} = (r_{Mg} + r_X)n_{Mg}n_X\Delta\chi^2 / (N_{Mg} + N_X) \quad (9)$$

where r_i and n_i are the ionic radius of species i and its oxidation state, $\Delta\chi^2$ is the square of the difference in the electronegativities between migrating cations and the counteranions of the lattice, and N_i is the number of atoms of the corresponding species in the unit cell of the crystal. Whereas the influence of the ionic radii and the oxidation or charge state of the ions on migration barriers has been discussed before (see, e.g., ref 52), we additionally quantify the degree of nonionicity, i.e., the softness of the ions, in the interaction of the cations and anions in these materials by $\Delta\chi^2$. All these factors enter in a multiplicative way in this descriptor.

For all considered Mg binary materials, the calculated migration barriers as a function of migration number (N_{migr})³³ are plotted in Figure 3b. The square of the electronegativity difference quantifies the role of the deviation from a purely ionic interaction between the migrating cation and the anions of the host lattice which contribute to the bonding in a nominally ionic crystal.^{32,33} We find a linear scaling between the migration number and the calculated migration barrier, giving the descriptor a predictive power with respect to the migration barriers of new binary compounds.³³ For the outliers from the linear scaling relation in Figure 3b, additional factors play a role such as the Pauli repulsion.⁵³

According to the calculations and an analysis of the migration number, MgF₂ and MgO are associated with high Mg migration barriers of above 1 eV, which is related to the strong ionic bonding characteristics reflected in the large difference in the electronegativity. In contrast, Mg₂Ge, with metallic bonding characteristics indicated by the small electronegativity difference, exhibits a very low migration barrier (less than 0.5 eV). The remaining Mg-halides, Mg-chalcogenides, Mg-pnictides, and Mg-tetrels have intermediate bonding characteristics between ionic and metallic bonding. MgS and MgSe, with an electronegativity difference of about 1.3, exhibit a barrier of 0.9 eV. Mg migration in MgCl₂, MgBr₂, and Mg₃N₂ with an electronegativity difference of 1.7 is hindered by a barrier of about 0.7 eV. Combining the results of the stability analysis shown in Figure 4 with the results for the ion mobility shown in Figure 3b, among all considered binaries the halides MgCl₂, MgBr₂, and MgI₂ represent a good compromise between a large electrochemical stability window with a sufficiently small migration barrier, making them promising candidates for coating materials in Mg batteries. The height of the migration barriers of all considered Mg binaries are in a good agreement with previously reported results²² where similar trends have been found.

Passing from Mg binaries to Mg ternary spinels with the general formula of MgB₂S₄, the compositional complexity increases to three different species. The spinel structure consists

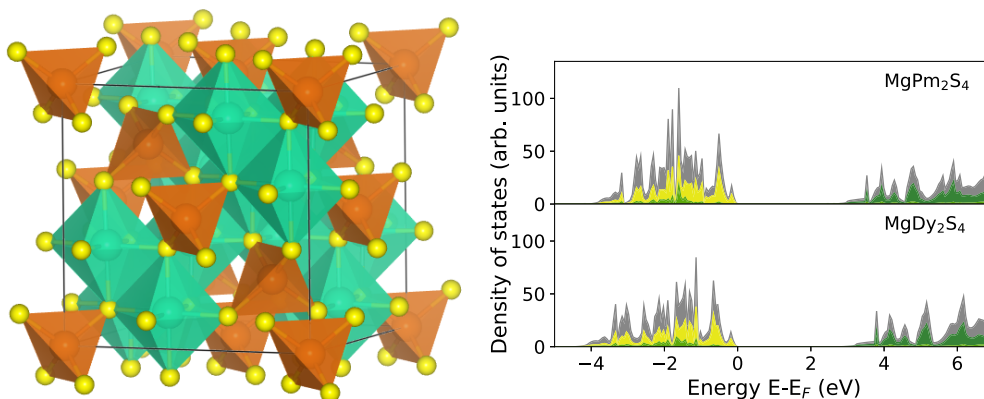


Figure 5. Structure of the MgB_2S_4 spinel. The Mg atoms (orange) occupy the tetrahedral sites, while the B species (spring green) only occupy octahedral sites. The yellow spheres denote the S^{2-} anions. The right graph shows the calculated density of states (DOS) using the HSE06 hybrid functional for MgPm_2S_4 and MgDy_2S_4 compounds. The total DOS is given in gray, and the projected DOS is shown in yellow for S- p orbitals and green for both Tm- d and Dy- d states.

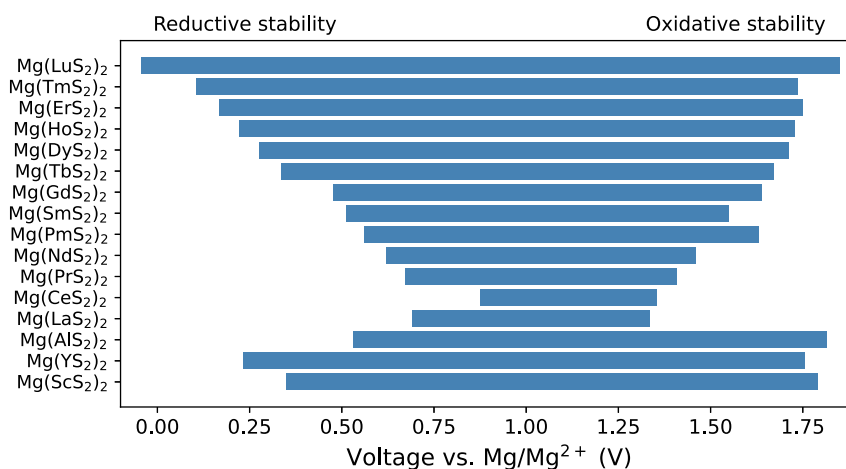


Figure 6. Electrochemical stability windows of the considered MgB_2S_4 compounds as a function of the voltages vs Mg metal.

of a cubic close packed array of S^{2-} anions in which the Mg cations occupy one-eighth of the tetrahedral holes and the B cations occupy half the octahedral holes (Figure 5). Structurally, a large number of vacant sites is available, and the open crystal structure, in principle, allows a migrating atom to move rather freely through the lattice.

Recently, the spinel framework was proposed as a potential candidate for solid electrolytes of multivalent ion batteries such as Mg due to the rather low activation energy for migration, E_a .^{28,30,32} On the atomic scale, the migration pathway of Mg^{2+} in a sulfide spinel structure starts from the energetically most favorable tetrahedral site and proceeds to the next-nearest neighboring tetrahedral site by passing the metastable octahedral site in a straight line. The stability of the Mg-ion in the tetrahedral site is lower than predicted from a pure electrostatic model due to the strong covalent nature of the Mg-S interaction.³²

We have addressed lanthanoid and empty d -shell sulfide spinels to find appropriate Mg conductors that balance stability and high ion mobility. Electronically, in these particular transition metal spinels the d -band occupancy is zero, resulting in a large band gap between the filled valence band, which is dominated by the sulfur p orbitals indicated in yellow in Figure 5, and the empty d -band (green) as the conduction band.

We have evaluated the electronic structure of all MgB_2S_4 spinel compounds employing the HSE06 hybrid functional. MgCe_2S_4 , MgEu_2S_4 , and MgYb_2S_4 represent no electronic band gap, while other spinel compounds can be classified into the midrange band gap materials (more than 2.5 eV), possessing a rather poor electronic conductivity, and can, thus, be regarded as insulating materials. Therefore, the first criterion necessary for the use as solid state electrolytes (SSEs) or coatings is satisfied in these structures.

The next step in proposing suitable and practical materials for the electrolyte phase is the assessment of stability limits in the low-potential magnesium-rich and high-potential magnesium-poor directions. For this purpose, the electrolyte stability windows of the considered ternary spinel phases have been determined using the Gibbs free energy of the phases according to eqs 4 and 5, as shown in Figure 6. The reductive stability reactions are determined by the triangle MgM_2O_4 - MgS - MS , whereas the oxidative stability is calculated using the metal sulfide phases MgM_2O_4 - M_2S_3 - MS . According to Figure 6, all calculated stability windows are smaller than 1.8 V. Among the considered candidates, those sulfide spinels with large ionic radii of the B cation (La, Ce, Pr, Nd, Pm, and Sm) display narrow stability windows due to the instability against Mg metal. The largest stability windows are found for the metals Lu, Y, and Sc.

Note that also the ionic radii r_i of the constituents have been used⁵⁴ to predict the stability of spinel compounds based on the so-called tolerance factor, τ , which is a dimensionless number based on the ratio of the sum of ionic radii of all ions (A, B, X):

$$\tau = \frac{\sqrt{3}(r_B + r_X)}{2(r_A + r_X)} \quad (10)$$

The tolerance factor is derived from the geometrical relationship between the different polyhedra being present in some materials including perovskites and garnets. A tolerance factor of less than one reflects the presence of compressed octahedra which is associated with the fact that the normal spinel structure becomes the most stable configuration. Table 2 collects, among other

Table 2. Calculated Migration Barriers (eV), Tolerance Factors (τ), and B-Cation Ionic Radii r_B (given in pm) of the MgB_2S_4 Normal Spinel Structure

Compound	r_B (pm)	Migration barrier (eV)	Tolerance factor (τ)
MgAl ₂ S ₄	67.5	0.484	0.803
MgSc ₂ S ₄	88.5	0.415	0.874
MgY ₂ S ₄	104.0	0.360	0.927
MgLa ₂ S ₄	117.2	0.478	0.972
MgPr ₂ S ₄	113.0	0.429	0.957
MgNd ₂ S ₄	112.3	0.398	0.955
MgPm ₂ S ₄	111.0	0.368	0.951
MgSm ₂ S ₄	109.8	0.357	0.947
MgGd ₂ S ₄	107.8	0.354	0.940
MgTb ₂ S ₄	106.3	0.353	0.935
MgDy ₂ S ₄	105.2	0.358	0.931
MgHo ₂ S ₄	104.1	0.365	0.927
MgEr ₂ S ₄	103.0	0.379	0.924
MgTm ₂ S ₄	102.0	0.386	0.920
MgLu ₂ S ₄	100.1	0.407	0.914

properties, the calculated tolerance factors τ of the spinel materials considered in this study. All values are within the range $0.8 < \tau < 1$, indicating that all compounds should be stable as spinels and thus producible.

In order to check the reliability of structure prediction according to the tolerance factor, a more accurate estimate of the stability of these spinel structures relative to competing polymorphs and competing compounds was investigated using the energy above the convex hull of stable compounds in each chemical space, E_{hull} . Stable compounds have $E_{hull} = 0$, and the

synthesizability of sulfides has been observed up to $E_{hull} = 0.05$ eV/atom.⁵⁵ In Figure 7a, the energies above the convex hull for all compounds considered in this structure are plotted as a function of the ionic radius of the B cation. First of all, it should be noted that the unit-cell volume of the spinel structure increases by substituting a larger B cation. For ionic radii of the B cation above about 110 pm, the energy above the convex hull in general becomes larger than 0.05 eV/atom. This indicates that larger ionic radii lead to a destabilization of the spinel structure and, thus, to a preference for non-spinel-type structures.

The different stability indicators can be assessed as follows: The tolerance factor, τ , gives a rough crystallographically based estimate for the stability of the spinel compounds using only ionic radii. The energy above the convex hull, E_{hull} , additionally yields the stability with respect to competing compound structures and polymorphs. Still, the electrochemical stability window appears to be the crucial quantity with respect to the stability of these materials as solid electrolytes and coating materials.

In order to additionally provide a general idea about the chemical trends in the migration energy barrier with respect to the size of the transition metals used in the spinel materials, in Figure 7b also the migration energy is plotted as a function of the B-cation ionic radii. The NEB method was applied to determine the migration barrier. A strong correlation between the B-cation ionic radius and the calculated migration barriers is observed with a pronounced minimum for radii between 100 to 110 pm, indicating a high Mg-ion mobility in this range. Thus, the choice of the transition metal B allows us to tune the ion mobility in the spinel compounds.

Next we consider the details of the Mg migration in more detail. In Figure 8, the energy profiles along the Mg migration path from the tetrahedral site across the octahedral site to the next tetrahedral site are shown. The tetrahedral site is the energetically most stable site for Mg in all considered compounds. The octahedral site corresponds to a local minimum for all compounds except for MgLa₂S₄, MgPr₂S₄, MgNd₂S₄, and MgPm₂S₄. Although increasing the B-cation size in sulfide spinels first leads to a decrease in the Mg²⁺ migration barrier, for radii larger than 1.1 Å such as in Pm, Nd, Pr, Ce, and La, the transition state energy rises again, as illustrated in Figure 7b, as a consequence of the fact that the octahedral site becomes energetically more costly,⁵⁶ finally even making the octahedral site to the transition state for migration. Interestingly, those

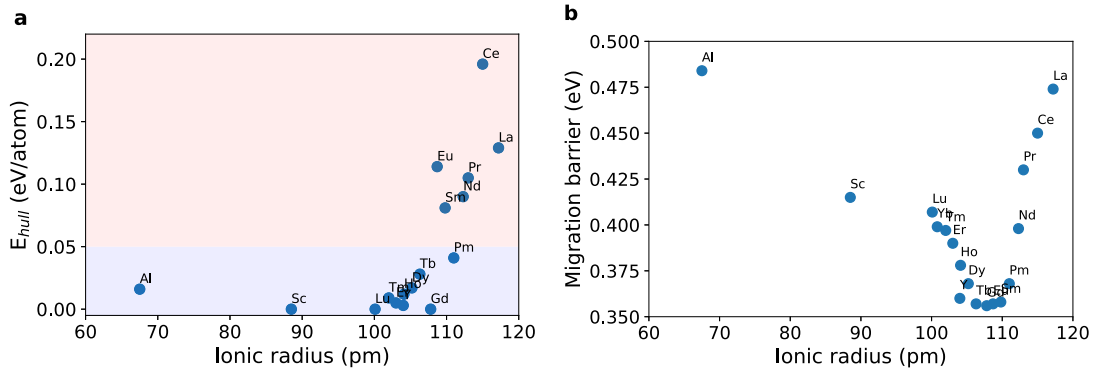


Figure 7. Dependence of the energies above the convex hull, E_{hull} , and the migration barriers as a function of the ionic radii of the B cation in sulfide spinels. (a) Energy above the convex hull E_{hull} in eV. The blue region represents the range of stable sulfide spinels whereas the red area corresponds to unstable compounds. (b) Calculated migration barriers (in eV).

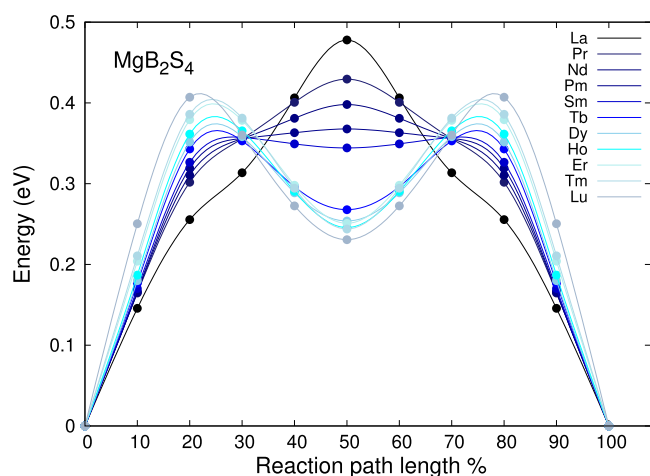


Figure 8. Mg^{2+} migration energy barriers (in eV) as a function of the reaction path coordinate derived from periodic DFT calculations combined with NEB for the single-ion migration between two tetrahedral sites across the octahedral site. The calculations are performed in the high-concentration limit, namely with a $\text{Mg}_{0.875}\text{B}_2\text{S}_4$ stoichiometry.

compounds in which the octahedral site becomes the transition state are unstable.

This correlation indicates that the size of the B cations plays a dominant role with respect to the height of the Mg-ion migration barriers as well as for the stability of the spinel compounds. The B-cation ionic radius is decisive for the equilibrium B–S bond length and thus also influences the strength of this bond. Qualitatively, enlarging the bonds should lower their bonding strength, which reduces the stability of the spinel compounds.

Note that, in spite of the variation in the height of the Mg migration barriers in the MgB_2S_4 spinels, the calculated barrier heights are all in the range between 0.35 and 0.49 eV, which makes them good ionic conductors.⁵² Furthermore, those of the compounds with B-cation radii smaller than 1.1 Å are also chemically stable so that one should be able to prepare these compounds. Still, all of them have electrochemical stability windows that are below 1.8 V, with the Lu, Y, and Sc spinel compounds having the largest electrochemical stability window.

In summary, the electrochemical stability windows of Mg binary and spinel sulfide compounds together with their Mg migration paths have been computed using DFT calculations in order to assess their feasibility as solid electrolytes or potential coating materials. Among the considered binaries, MgBr_2 , MgI_2 , and MgCl_2 exhibit a good stability against the highly reductive Mg metal anode as well as an acceptable Mg^{2+} mobility. Furthermore, our study highlights the critical role of the Pauling electronegativity for the band gap and the ionic conductivity of these binary compounds. For the sulfide spinel compounds, the B-cation ionic radius has been identified to play a dominant role with respect to the stability and Mg migration energy barriers. All considered compounds exhibit sufficiently low Mg migration barriers, but only MgLu_2S_4 , MgY_2S_4 , and MgSc_2S_4 have been found to be electrochemically stable over a voltage range close to 2 V. We trust that these insights will serve as valuable design guidelines for developing fast Mg conducting solid materials with improved properties.

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Notes

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