Computational studies on magnesium spinel’s [MgY$_2$S$_4$ and MgY$_2$Se$_4$]

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Abstract: The need for novel battery cathode materials is growing every day, and an ongoing study on magnesium (Mg) has intensified due to its many advantages such as its abundance on earth, low cost, and ease of handling. Furthermore, Mg$^{2+}$ has the advantage of doubling the overall charge per ion compared to Li$^+$ and boosting the energy density of a battery. The major challenge, is the identification of cathode materials that demonstrate capacities and voltages similar to lithium-ion systems. In this study, the first principle-based calculations were used to investigate the stability of discharge products for MgY$_2$S$_4$ and MgY$_2$Se$_4$ structures employing density functional theory (DFT) through VASP within the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) exchange-correlation. The computed elastic constants indicate that the structures are mechanically stable. We found that MgY$_2$S$_4$ and MgY$_2$Se$_4$ structures are electronically stable semi-conductors with direct band gaps of 1.79 and 1.27 eV observed in the density of states, respectively. No negative vibrational frequencies are observed in all directions in the phonon dispersion curves, which indicates vibrational stability. The findings of this work aim to improve the production, research, and development of solid electrolyte magnesium-ion batteries.

1. Introduction

The production of magnesium-ion batteries (MBs) seems to be a workable solution to get beyond the restrictions and issues associated with energy density that lithium-ion technology is currently dealing with, such as explosions due to overheating and short-circuiting [1]. These rechargeable magnesium-ion batteries are promising to be the next battery technology addressing the future electrical energy storage for large-
scale mobile and stationary devices. This is due to the high environmental abundance of magnesium metal and the divalent character of magnesium ion [2, 3]. Using magnesium (Mg) metal directly as the anode offers various advantages; these include battery safety and long lifespan that can be improved since magnesium electrodeposition occurs without the production of dendrites, which is a common problem with zinc or lithium metal anodes [4]. Oxide spinels have been studied for Mg systems; however, progress in this area has been constrained by difficulties in locating appropriate electrolyte systems as well as poor mobility in many spinels [3].

Hence, the development of competitive magnesium-ion batteries is plagued by the existing notion of poor magnesium mobility in solids. The theoretical predictions [5] indicate that high magnesium ion mobility is possible in other chalcogenides spinel’s, opening the door for the realization of other magnesium solid ionic conductors and eventually the development of an all-solid-state magnesium battery (ASSMBs). Additionally, studies of MgSc2S4 and MgIn2S4 as solid electrolytes demonstrate that high mobility can be attained experimentally [5]. However, a brief overview of the more established and well-known subject of lithium batteries (LBs) would probably serve as a good introduction to the topic of magnesium electrochemistry [6]. Hence, first principle based calculations were employed in this study to investigate the stability properties of magnesium yttrium sulphide (MgY2S4) and magnesium yttrium selenium (MgY2Se4) solid electrolytes.

2. Methodology

Computational computations were carried out based on the density functional theory (DFT) through Vienna ab initio simulation package (VASP) code [7] within the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) exchange-correlation. Energy cut-off of 500 eV and Monkhorst and Pack k-points mesh parameter of 5x5x5 were used throughout the study since it was sufficient to converge the total energy of the systems. The above mentioned cut-offs and the k-point mesh were utilised in calculating the lattice parameters, heats of formation, the elastic constants, density of states, as well as the phonon dispersion curves. The phonon code [8] embedded in MedeA [9] application was employed in order to run the calculations of phonon dispersion curves. The geometric structures of MgY2S4 and MgY2Se4 were fully relaxed until the total energy and the Hellmann-Feynman force were converged to 1x10^-6 eV and 0.01 eV/Å, respectively.

3. Results

3.1. Structural and thermodynamic properties

In fig. 1, below, we show the structures of magnesium yttrium sulphide (MgY2S4) and magnesium yttrium selenide (MgY2Se4), respectively. Each of the two structures has 56 atoms that belong to the Fd-3m space group. In both structures, magnesium atoms occupy 8a tetrahedral sites; yttrium atoms occupy 16d octahedral sites; and sulphide and selenide atoms tend to form a cage and occupy the 32e sites.
Sulphide and selenide atoms tend to form atoms occupy 8a tetrahedral sites; yttrium atoms occupy 16d octahedral sites; and has 56 atoms. In f.

Structural and thermodynamic properties

Methodology

Computational computations were carried out through ab initio first principle based on the VASP code. The phonon dispersion curves. The phonon parameters, heats of formation, the elastic constants, density of states, as well as the mentioned cut.

According to the heats of formation, the MgY2S4 structure is found to be the most stable when compared to the MgY2Se4 structure because it has the least negative value, in other words, it is more thermodynamically stable.

Table 1. The equilibrium lattice parameters and heats of formation (\(\Delta H_f\)) of MgY2S4 and MgY2Se4 structures.

<table>
<thead>
<tr>
<th>Structures</th>
<th>Lattice parameters (Å)</th>
<th>Volume(Å³)</th>
<th>(\Delta H_f) (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgY2S4</td>
<td>10.63</td>
<td>1200.14</td>
<td>-0.23</td>
</tr>
<tr>
<td>MgY2Se4</td>
<td>11.12</td>
<td>1375.04</td>
<td>-0.21</td>
</tr>
</tbody>
</table>

3.2. Elastic constants

In this work, the elastic constants are used to determine the response of our crystal structures to external forces, and they play an essential part in defining their strength.
Since our structures are cubic, the elastic constants are therefore three namely, $C_{11}$, $C_{12}$, and $C_{44}$. In table 2, we have shown the values of our two structures, MgY$_2$S$_4$ and MgY$_2$Se$_4$, with their $C'$ values. The bulk, shear, and Young’s modulus are represented in table 2 as well.

Table 2: Elastic constants, Bulk, Shear, Young’s Modulus and the B/G ratios for MgY$_2$S$_4$ and MgY$_2$Se$_4$ structures.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>$C'$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgY$_2$S$_4$</td>
<td>85.55</td>
<td>48.02</td>
<td>30.08</td>
<td>18.77</td>
</tr>
<tr>
<td>MgY$_2$Se$_4$</td>
<td>69.62</td>
<td>42.03</td>
<td>24.28</td>
<td>13.80</td>
</tr>
</tbody>
</table>

The two structures, MgY$_2$S$_4$ and MgY$_2$Se$_4$, satisfied the following requirements for the mechanical stability of a cubic system, as stated in [10]:

$$C_{44} > 0, \quad C_{11} > |C_{12}| \quad \text{and} \quad C_{11} + 2C_{12} > 0,$$

where the only three independent elastic constants are $C_{11}$, $C_{12}$ and $C_{44}$. All computed elastic constants are positive, and the $C'$ values are positive, which indicates that both structures are mechanically stable. Pugh's ratio $k$ serves as a measure that characterizes ductility [11]. It is defined as $k = B/G$, and if the value of $B/G$ exceeds 1.75, the structure is considered to exhibit ductility; otherwise, it is considered brittle. Therefore, in table 2, it is evident that both structures exhibit ductility because the $B/G$ ratio surpasses the threshold of 1.75. Examining the bulk, shear, and Young's moduli values of the MgY$_2$Se$_4$ structure, it becomes evident that they are lower in comparison to those of MgY$_2$S$_4$. This suggests that MgY$_2$Se$_4$ exhibits greater resistance to volume changes within its crystal structure and is less susceptible to deformation, aligning with our anticipated expectations. The ductility of the MgY$_2$Se$_4$ structure implies that it exhibits greater ductility when compared with MgY$_2$S$_4$.

### 3.3. Density of States

We have calculated the density of states (DOS) as it is a fundamental concept in the field of solid-state and condensed matter physics. It plays a crucial role in understanding the electronic properties of materials, such as metals, semiconductors, and insulators. The DOS for conduction and valence bands is determined by both the likelihood of occupancy at a specific energy level and the availability of states that can be occupied at that energy [12]. In fig. 2, we illustrate the density of states for the MgY$_2$S$_4$ and MgY$_2$Se$_4$ structures. As depicted in the charts provided, we are illustrating the individual contributions of magnesium (Mg), yttrium (Y), sulphur (S), and selenium (Se) atoms from a magnified perspective.

We note that our two systems are semiconductors, with the direct energy band gap for the MgY$_2$S$_4$ system measuring 1.79 eV, whereas for MgY$_2$Se$_4$, the direct band gap is 1.27 eV. The MgY$_2$S$_4$ system has a larger band gap, which implies that it
requires higher or more energy (shorter wavelength) photons to promote electrons from the valence band to the conduction band. This suggests that MgY\textsubscript{2}S\textsubscript{4} is less absorptive in the visible light range compared to MgY\textsubscript{2}Se\textsubscript{4}. The electrical resistivity of MgY\textsubscript{2}Se\textsubscript{4} is lower than that of MgY\textsubscript{2}S\textsubscript{4} due to its narrower band gap, which also means that it does not require much energy to transfer electrons from the valence band to the conduction band.

![Density of States](image)

**Fig. 2.** The Density of States for a) MgY\textsubscript{2}S\textsubscript{4} and b) MgY\textsubscript{2}Se\textsubscript{4}.

### 3.4. Phonon dispersion curves

It is very crucial to calculate the phonon dispersion curves, as they play an important role in the branches of physics and engineering since they can be used to determine the physical properties of solid-like electrical conductivity, thermal expansion, and the vibrational stability of structures [13]. The two different kinds of phonon modes are optical and acoustic. When negative acoustic (soft) modes are absent, vibrational stability is observed instead of instability. We notice from the phonon dispersion curves shown in fig. 3 below that neither the MgY\textsubscript{2}S\textsubscript{4} and MgY\textsubscript{2}Se\textsubscript{4} structures exhibit any negative (soft) modes or vibrations along the Brillouin zone direction (Γ-direction), proving that the structures are vibrationally stable. The calculated elastic constant $C'$ values were discovered to be positive, demonstrating stability and agreeing well with the computed phonon dispersion curves.
4. Conclusion

First-principle based calculations were successfully employed to investigate the structural, thermodynamic, mechanical, and electronic properties of magnesium spinels’ [MgY$_2$S$_4$ and MgY$_2$Se$_4$]. It is observed that the lattice parameters of MgY$_2$Se$_4$ are greater than those of the MgY$_2$S$_4$ structure, which implies that it has a larger unit cell dimension, is less dense, and has a more open crystal structure. The MgY$_2$S$_4$ structure is found to be thermodynamically stable with the least negative value of heats of formation. The calculated elastic constants are found to be all positive and stable while meeting the mechanical stability criteria for the cubic structure. They also suggest that the MgY$_2$Se$_4$ structure is more ductile compared to MgY$_2$S$_4$. The former has greater resistance to volume changes within its crystal structure and is less vulnerable to deformation. In the density of states (DOS) graphs, we found that MgY$_2$S$_4$ and MgY$_2$Se$_4$ are electronically stable semi-conductors with direct band gaps of 1.79 and 1.27 eV at Fermi energy, respectively. Finally, the phonon dispersion curves demonstrate that both structures are vibrationally stable because no negative vibrations were seen in the directions of the Brillouin zone (Γ-direction). The MgY$_2$Se$_4$ structure shows to be most favourable when compared to MgY$_2$S$_4$. One may need to continue and do R&D on it; perhaps it might be the solid electrolyte the world has been waiting for to potentially improve magnesium-ion batteries.

5. Acknowledgements

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References