Effects of Mg substitution on electronic properties of CaF$_2$

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Abstract. We investigated the phase transitions of CaF$_2$, using the state-of-the-art density functional theory. The calculations show that the fluorite structure, with the space group Fm3m, transforms into the cotunnite structure, with the space group Pnma, at 8 GPa. The electronic band structure of the Pnma-CaF$_2$ structure can be classified as an insulating phase with a wide bandgap, and the bandgap decreases under pressure above 70 GPa. Also, we proposed the Ca/Mg-substituted fluorides Mg$_x$Ca$_{1-x}$F$_2$, using the cluster expansion technique which is commonly used to study alloys. We found that the Mg$_{0.25}$Ca$_{0.75}$F$_2$ compound with a Pm structure is stable at 70 GPa. The results of the electronic band structure reveal that the substitution of Mg enhances the bandgaps of the Mg$_{0.25}$Ca$_{0.75}$F$_2$ compounds under pressure above 70 GPa, compared with those of CaF$_2$.

1. Introduction

The group-II difluorides, i.e. CaF$_2$ and MgF$_2$, have attracted much attention due to their electronic properties and structural stability. The CaF$_2$ compound has many interesting applications, for example, it is used for internal pressure calibration [1], it can be used as a glass due to its high transmittance [2], it is one of the best candidates for an FeSe thin film substrate since it is an oxygen-free compound, unlike other oxygen-based substrates [3]. The stacking of FeSe and CaF$_2$ also increases the superconducting transition temperature of FeSe. Under pressure, the phase transformation of CaF$_2$ is in the following order [4]: Fm3m (0 GPa) $\rightarrow$ Pnma (8.1 GPa) $\rightarrow$ P6$_3$/mmc (278 GPa). The phase transitions of CaF$_2$ from Fm3m (fluorite) to Pnma (cotunnite) have been confirmed experimentally by Dorfman et al. [5]. The band structure calculations indicate that the high-pressure phases of CaF$_2$, i.e. Pnma and P6$_3$/mmc, are insulators. Wu et al. showed that the bandgap of CaF$_2$ depends on the pressure [6]. The bandgap increases as pressure increases. However, beyond 70 GPa, the bandgap of CaF$_2$ starts to slightly collapse [6]. Several previous studies have investigated the effects of doping, such as Pr$^{3+}$ [7, 8], Nd$^{3+}$ [9, 10], and Yb [11], in the CaF$_2$ compound. They found that most doped CaF$_2$ compounds have a decreasing band gap under pressure.

The MgF$_2$ compound is also of interest as it has high transmittance, and can be used in glass manufacturing [12]. Under the ambient conditions, MgF$_2$ adopts the rutile P6$_3$/mmc structure. Under
pressure, the phase transformation of MgF₂ is in the following sequences [13]: P4/ mmm (0 GPa) → Pbn (9.4 GPa) → Pa3 (15.4 GPa) → Pbca (39.6 GPa) → Pnma (44.1 GPa). In this work, we are particularly interested in the Pnma-MgF₂ phase, as it is similar to the Pnma-CaF₂ phase.

As CaF₂ and MgF₂ share the common Pnma structure under high pressure, the Ca/Mg-substituted fluorides, Mg₇Ca₁₋ₓF₂, should be a natural choice for the modification of these difluorides. Sukmas et al. used a similar Ca/Mg-substituted technique to improve the superconductivity of some metal hydrides under high pressure [14]. In this work, the wide bandgap under pressure is of particular interest. We showed that the Ca/Mg-substituted technique can be used to prevent these difluorides bandgap from collapsing under high pressure.

2. Calculation methods

We used the density functional theory (DFT), as adopted in CASTEP [15], to optimize and calculate electronic properties of CaF₂ and MgF₂ in the Pnma phase. The Pnma unit cell is shown in figure 1 (a). To determine the ground-state energy of the optimized structures, the Generalized Gradient Approximation (GGA) developed by Perdew-Burke-Ernzerhof (PBE) [16] and the ultrasoft pseudopotential were selected as the exchange correlation functional and pseudopotential, respectively. We chose the optimum kinetic cutoff energy of 500 eV and k-point grid spacing of 2π×0.04 Å⁻¹. We confirmed the phase transition of CaF₂ by plotting the enthalpy difference between the Fm̅3m and Pnma phases of CaF₂ with pressure, as depicted in figure 1 (b). Our calculations are also consistent with those of Cui et al. [4]. The optimized structure of CaF₂ was then used to calculate the band structures and the density of states in the range of 0-100 GPa.

Figure 1. (a) The Pnma unit cell of CaF₂. (b) The enthalpy difference between the Fm̅3m and Pnma phases of CaF₂ as a function of pressure (black squares). The enthalpies of the Pnma phase at various pressures are set as references, thus the enthalpy difference of the Pnma phase is zero at every pressure, as denoted by red dots. The transition from the Fm̅3m to the Pnma phases occur at around 8 GPa, in good agreement with the previous work [4].

Next, we selected the optimized CaF₂ and MgF₂ structures at 70 GPa as inputs for searching for a stable structure of Mg₇Ca₁₋ₓF₂, using the Alloy-Theoretic-Automated Toolkit (ATAT) [17]. We chose the pressure of 70 GPa as it marks the starting point of the bandgap collapsing of CaF₂, as shown in figure 2 (a). Firstly, several “known structures (known str)” are generated by the ATAT, and their energy are evaluated by the DFT (red dots). Some energy parameters are extracted from these “known str” for the cluster expansion method. Then, the “Predicted” structures (black square dots) are generated and they energies can be estimated from the cluster expansion. This step is very quick and suitable for searching a really large number of samples. After searching the samples of various structures and compositions, the result is the lowest-energy structure. This structure is then optimized by using the
DFT to confirm that it is the “known ground state (known gs)” (blue triangles). The ATAT result shows that the most stable composition at 70 GPa is Mg$_{0.25}$Ca$_{0.75}$F$_2$ with a Pm structure, as shown in figure 2 (b). The optimized Pm structure of Mg$_{0.25}$Ca$_{0.75}$F$_2$ is shown in figure 2 (c). The lattice parameters at this pressure are $a = 6.2393$, $b = 3.1530$, and $c = 5.1317$, where $\alpha = \gamma = 90^\circ$, and $\beta = 91.3989$. Then, we continued by using this structure as an input for the structure optimization via CASTEP [15], and calculated the band structures and the density of states of the optimized Mg$_{0.25}$Ca$_{0.75}$F$_2$ structure in the range of 0-100 GPa.

Figure 2. (a) The Bandgaps of CaF$_2$ (black squares and red circles) and Mg$_{0.25}$Ca$_{0.75}$F$_2$ (blue triangles) as a function of pressure. (b) The plot of energy from a large number of samples of the varying elemental composition of Mg$_x$Ca$_{1-x}$F$_2$ at 70 GPa from the ATAT [17]. (c) The unit cell of Mg$_{0.25}$Ca$_{0.75}$F$_2$ at 70 GPa, where F is represented by grey spheres, Ca by blue spheres, and Mg by an orange sphere.

Figure 3. The projected density of states of Mg$_{0.25}$Ca$_{0.75}$F$_2$, (a) at 0 GPa and (b) at 70 GPa.

3. Results and discussion
We found that Mg$_{0.25}$Ca$_{0.75}$F$_2$ with a Pm structure is the most stable composition. The Pm unit cell is shown in figure 2 (c). The bandgap as a function of pressure of the Fm3m and Pnma phases of CaF$_2$ is shown in figure 2 (a). We found that CaF$_2$ is a wide-bandgap insulator under pressure, and the bandgap increases in the range of 0-70 GPa, but slightly collapses between 70-100 GPa. This is in good agreement with the theoretical results of Wu et al. [6]. The bandgap as a function of pressure of Mg$_{0.25}$Ca$_{0.75}$F$_2$ is also shown in figure 2 (a), compared with that of CaF$_2$. It is also a wide-bandgap insulator under
pressure, but the bandgap is slightly less than that of CaF$_2$ at pressure less than 70 GPa. The bandgap of Mg$_{0.25}$Ca$_{0.75}$F$_2$ increases as pressure increases, and is greater than that of CaF$_2$ in the pressure range of 70-100 GPa. From the projected density of states of Mg$_{0.25}$Ca$_{0.75}$F$_2$ at 0 GPa, the valence band maximum (VBM) is dominated by the p-band of F, whereas the conduction band minimum (CBM) is dominated by the s-band of Mg and Ca. As shown in figure 3 (a), at 70 GPa, the VBM is still dominated by the p-band of F, whereas the CBM is dominated by the s-band and p-band of Mg, as shown in figure 3 (b). Our results indicate that at this pressure the bandgap behavior is controlled by the electronic states of Mg. Thus, the Mg substitution into CaF$_2$ helps prevent the collapsing bandgap, as occurred in the pure CaF$_2$ compound, beyond 70 GPa.

4. Conclusion

We performed the cluster expansion technique to confirm the thermodynamically stable structure of Mg$_{0.25}$Ca$_{0.75}$F$_2$, which is a Pm3m structure. This structure was subsequently used to calculate the band structure and the projected density of states. Our results reveal that around 70 GPa the electronic states of Mg are dominated the CBM. Thus, they control the bandgap of Mg$_{0.25}$Ca$_{0.75}$F$_2$ from 70 GPa onwards. Furthermore, the Mg substitution into CaF$_2$ helps prevent the collapsing bandgap of this fluoride compound under high pressure above 70 GPa. As the relation between bandgap and pressure is almost linear, we suggest that our Ca/Mg-substituted fluoride can be used as an internal pressure calibrator in a pressure cell.

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