High-Pressure Phases and Properties of the Mg$_3$Sb$_2$ Compound

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ABSTRACT: Pressure always plays an important role in influencing the structure and electronic properties of materials. Here, combining density function theory and structure prediction algorithm, we systematically studied the Mg$_3$Sb$_2$ system from its phase transition to thermodynamic and electronic properties under high pressure. We find that two novel phases, namely Cm and C2/m, are stable under high pressure. Calculation results of phonon dispersions showed that both novel phases have no imaginary frequency, which indicates that the novel phases are thermodynamically stable. Due to the larger ionic radius of Sb compared to N, P, and As elements, the Mg$_3$Sb$_2$ compound shows a different electronic property at high pressure. The electronic calculations show that the novel phases of Cm and C2/m of Mg$_3$Sb$_2$ possess metallic behavior under high pressure. These results provide new insights for understanding the Mg$_3$Sb$_2$ compound.

INTRODUCTION

Pressure is one of the most powerful tools, which is frequently used to find and design novel materials with unique properties, as it can influence the geometric configuration, interatomic electrostatic interactions, distance of bonding, and electronic orbitals. For decades, scientists have found and synthesized numbers of materials under high pressure, which are not available at ambient condition.

The A$_3$B$_2$-type compounds are usually formed by group II alkaline metal elements and group V elements. As one member of the A$_3$B$_2$-type family, the ground state of Mg$_3$Sb$_2$ compounds at ambient condition possess a typical cubic anti-bixbuite symmetry of the minerals, like (Fe, Mn)$_2$O$_3$. So far, numerous studies both on experiment and theory have been done on these compounds due to their large band gaps. Scientists have shown that the Mg$_3$N$_2$ compound has several phase transitions from ambient condition to high pressure. In 2017, a theoretical work reported that the Mg$_3$P$_2$ compound has three stable phases under extreme conditions, while the compound of Ca$_3$N$_2$ in the A$_3$B$_2$-type family, undergoes several phase transformations (like Ia$_3$, R3c, P6$_3$/m, P2$_1$/m, P311, and I43d) from experimental and theoretical studies. Recently, Yang, et al. studied the phase transformations and electronic properties of Mg$_3$As$_2$ under high pressure and they found that two novel semiconductor phases are stable under high pressure. As one member of the A$_3$B$_2$-type family, Mg$_3$Sb$_2$ has attracted much focus on its structure configuration and electronic properties. The Mg$_3$Sb$_2$ compound adopts Ia$_3$ and P311 symmetry at ambient conditions and high pressure, which are provided by early works. Specially, the P311 phase of Mg$_3$Sb$_2$ attracts much attention for its good performance in the thermoelectric material field.
RESULTS AND DISCUSSION

Starting from structural prediction of the Mg₃Sb₂ system with a suitable unit-cell size (the maximal formula unites is eight due to the restriction of computer resource) at pressures of 0, 20, 50, and 100 GPa, respectively. Then, we made accuracy structure relaxation for the selected target structures (at least 10 structures that we chose in each prediction). We calculated the relative enthalpy of all structures of the Mg₃Sb₂ compound relative to the P₃m₁ phase as a function of pressure, which is illustrated in Figure 1. In addition, we considered some metastable structures with similar energies and the other A₃B₂ (e.g. Mg₃N₂, Mg₃P₂, and Mg₃As₂) stable phases, which act as prototype structures for this system. From our calculation, we conclude that the ground state structure of Mg₃Sb₂ adopts the Ia3̅ symmetry at ambient conditions. With the pressure increasing to 0.25 GPa, a trigonal phase with P₃m₁ becomes stable in energy. This phenomenon is consistent with the previous study and also occurred in the sister systems like Mg₃P₂ and Mg₃As₂. Interestingly, when the pressure increases to 5 GPa, we predict that a novel monoclinic phase with the Cm̅ symmetry becomes stable. However, this novel phase is quickly destabilized by pressure and transformed into another monoclinic phase with the C2/m symmetry. The C2/m structure will be stable in large pressures ranging from 12.7 to 100 GPa, which is the maximum pressure we simulated in this work. These results also checked by using SCAN functional. The results show that the phase transition sequence is the same when compared to PBE calculations. Only the transition pressures are slightly shifted. For example, the P₃m₁ phase transformed into the Cm̅ phase at about 5 GPa for PBE and at about 6 GPa for SCAN. These slight differences cannot change our main results and provide strong support for our previous study. The results are shown as Figure S1 in the Supporting Information.

Figure 2 shows four novel crystal phases of Mg₃Sb₂, which are predicted in this work. At ambient conditions, the Ia3̅ structure is the ground-state phase for the Mg₃Sb₂ compound, which has a well-known configuration as shown in Figure 2a.

The Mg–Sb bond length in this interesting configuration is about 2.87–3.94 Å and slightly larger than that of Mg₃As₂ (about 2.62–2.73 Å). This is mainly caused by the larger ionic core of Sb than that of the As atom. The primitive cell of the Ia3̅ phase contains eight formula units with the Mg atoms located in the 48c Wycko position, while the Sb atoms are located in the 8b and 24d positions. The P₃m₁ phase is stable in the pressure range of 0.25 to 5 GPa, and the structure character is shown in Figure 2b. It is clearly found that Mg atoms and Sb atoms form several diamond surfaces, which are connected with each other and form a spatial three-dimensional network configuration. The Sb atom behaves as a six coordination in this phase, while the Mg atom is connected with four neighboring Sb atoms. There are two kinds of Mg atoms in its primitive cell occupying in 2d and 1a Wycko positions. Meanwhile, Mg atoms are only located at the 2d position. The distance between the Mg and Sb atoms is about 2.82–3.06 Å. These results are very consistent with other known informations that are collected by the Materials Project database. The Cm̅ phase has an interesting structural configuration as shown in Figure 2c with the bond lengths of Mg–Sb being between 2.74 and 2.94 Å at 8 GPa. This structure is formed by several tetrahedrons and rhombuses, which are combined with shared Sb atoms. Figure 2d shows the C2/m phase of Mg₃Sb₂, which contains two formula units in its primitive cell. This novel phase is very interesting as its crystal configuration contains several hexagons and rhombuses, which are in the same distorted face and are connected to each other with sharing atoms. The chemical bond between the Mg atom and Sb atom is about 2.65–2.85 Å at the pressure of 20 GPa. The relaxed structural informations of these four phases are listed in Table 1. Through our calculation, we determined that the clear phase transformation of the Mg₃Sb₂ compound. The clear sequence is shown below: Ia3̅ → P₃m₁ (at 0.25 GPa) → Cm̅ (at 5 GPa) → C2/m (12.7 GPa). By comparing to the

Figure 1. The relative enthalpy between the different structures of each formula for the Mg₃Sb₂ compound varies with pressure relative to the P₃m₁ structure.

Figure 2. Crystal structures of Mg₃Sb₂ (green, Mg; black, Sb). (a) Ia3̅ phase at ambient pressure. (b) P₃m₁ phase at 2 GPa. (c) Cm̅ phase at 8 GPa. (d) C2/m phase at 30 GPa.
Table 1. Configuration Parameters of Ia3, P3m1, Cm, and C2/m Phases of the Mg3Sb2 Compound in Different Conditions

| pressure (GPa) | space group | lattice parameters | atomic coordinates (fractional) |
|---------------|-------------|--------------------|---------------------------------|
| 0             | Ia3         | \( a = b = c = 13.40 \text{ Å} \) Mg (2a) (0.38321, 0.39949, 0.37748) | \( \alpha = \beta = \gamma = 90^\circ \) |
|               |             | \( c = 7.15 \text{ Å} \) Mg (1a) (0.00000, 0.00000, 0.00000) | \( \alpha = \beta = 90^\circ, \gamma = 120^\circ \) |
| 2             | P3m1        | \( a = b = 4.53 \text{ Å} \) Mg (2a) (0.33333, 0.66667, 0.63137) | \( c = 7.15 \text{ Å} \) Mg (2a) (0.33333, 0.66667, 0.22282) |
| 8             | Cm          | \( a = 15.04 \text{ Å} \) Mg (2a) (0.29007, 0.50000, 0.37780) | \( \beta = 117.28^\circ \) |

Figure 3. Lattice constants and volume of the Mg3Sb2 system as a function of pressure.

Figure 4. Phonon dispersions of Mg3Sb2 for (a) the Ia3 phase at ambient pressure, (b) the P3m1 phase at 2 GPa, (c) the Cm phase at 8 GPa, and (d) the C2/m phase at 20 GPa.

In order to determine the thermodynamic stability of each phase, the phonon dispersion at its stable pressure point is calculated theoretically as shown in Figure 4. From the figure, we can conclude that all the phases of Mg3Sb2 are mechanically stable as there is no imaginary phonon frequency in all the Brillouin zone. We also checked the thermodynamic stability of these phases under ambient pressure. The results show that Ia3 and P3m1 phases of Mg3Sb2 are dynamically stable at ambient conditions, while for Cm and C2/m phases, their phonon dispersions have imaginary values, which reveal that they are unstable at ambient pressure. The results are shown as Figure S2 in the Supporting Information. Figure 5 shows the electronic band structures and the projected density of states for the four structures of Mg3Sb2 in their relative pressure. Note that all of the calculations were carried out in the PBE level, which always underestimates band gap, as we all know. Our calculations show that the Ia3 and P3m1 phases of Mg3Sb2 exhibit semiconductor properties with a band gap of 1.42 eV at ambient conditions and 0.86 eV at 0.25 GPa. This also

other three magnesium compounds, Mg3N2 (Ia3 → C2/m (at 20.6 GPa) → P3m1 (at 67 GPa)), Mg3P2 (Ia3 → P3m1 (at 2.5 GPa) → P63/mmc (at 35 GPa) → C2/c (at 65 GPa)) and Mg3As2 (Ia3 → (at 1.3 GPa) P3m1 → (at 12 GPa) C2/m → P\( \bar{I} \) (at 30 GPa)), we can find that the phase transition pressure point of Mg3Sb2 is earlier than the other three A3B2 compounds and can also make a conclusion that large atomic radii facilitate structural phase transitions for Mg3X2 (X = N, P, As, Sb). Another finding is that the high pressure and ionic radius both influence the structural configuration for different systems. For example, the Mg3N2, Mg3P2, Mg3As2, and Mg3Sb2 systems share the same ground state at ambient conditions, while at high pressure, their stable phases vary from system to system.

The structure parameters and cell volumes as a function of pressure of the four phases for the Mg3Sb2 compound are calculated, as shown in Figure 3. The results reveal that all the phase transitions belong to the first-order nature, as the volume collapsed at the phase transition. This phenomenon also occurred in its sister systems, like Mg3P2 and Mg3As2.11,19 This can regard as a common character of the A3B2 compounds under high pressure.
indicates that the band gap is getting smaller and smaller driven by pressure. When the pressure above 5 GPa, the semiconductor phase \( P3\bar{1}l \) transforms into a metallic phase \( Cm \). This unique phenomenon is the first time to occur in Mg\(_x\)X\(_2\) magnesium and may be mainly caused by the larger ionic radius of Sb compared to N, P, and As atoms and high compression.

**CONCLUSIONS**

In summary, using first-principle swarm-intelligence structure search, we investigate systematically the stability and electronic properties of Mg\(_3\)Sb\(_2\). We identified two hitherto unknown phases stabilized at a wide pressure range that are readily available for experimental synthesis. All the phases of Mg\(_3\)Sb\(_2\) from ambient to high pressure are confirmed, including \( Ia\bar{3}, P3\bar{1}l, Cm, \) and \( C2/m \). At low pressures, the stable phases of Mg\(_3\)Sb\(_2\) are \( Ia\bar{3} \) and \( P3\bar{1}l \). There is a novel metallic phase \( Cm \) that is stable from about 5 to 12.7 GPa. With the increasing pressure, the \( Cm \) phase will transform into another metallic phase \( C2/m \) at around 12.7 GPa. The phase transformation sequence of Mg\(_3\)Sb\(_2\) is \( Ia\bar{3} \rightarrow P3\bar{1}l \) (at 0.25 GPa) \( \rightarrow Cm \) (at 5 GPa) \( \rightarrow C2/m \) (12.7 GPa). Their mechanical stability is confirmed by the phonon calculations. At lower pressures, the \( Ia\bar{3} \) and \( P3\bar{1}l \) phases are semiconductors with a narrow band gap. However, when the pressure increases, the metallic phases \( Cm \) and \( C2/m \) are more stable under high pressure ranges. This is the first time that this phenomenon occurred in the Mg–Sb system. These results show a remarkable phase transition of Mg\(_3\)Sb\(_2\) and can serve as an important guide for further experimental studies of this compound.

**METHODS**

We start with structural prediction of the Mg\(_3\)Sb\(_2\) compound by using the CALYPSO method with the cells ranging from 2 to 8 formula units (f.u.) at 0, 50, and 100 GPa. Each prediction runs about 40 generations to ensure generating at least 1200 structures. The target structures that we selected from prediction were accuracy optimized by Kohn–Sham density function theory, within the projector augmented wave (PAW) method as implemented in the Vienna ab initio simulation package (VASP code) and with the Perdew–Burke–Ernzerhof (PBE) approximation to the exchange-correlation functional. The cutoff energy of all the calculations was set to 600 eV, and the K meshes used Monkhorst–Pack grids with the density of 0.03 Å\(^{-1}\) to reach the convergence of better than 1 meV per atom. We computed the phonon dispersions of all the novel phases by using a phonopy program.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04797.

Relative enthalpy of Mg\(_3\)Sb\(_2\) compounds (SCAN) and the phonon dispersions of Mg\(_3\)Sb\(_2\) compounds at ambient pressure (PDF)

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Notes
The authors declare no competing financial interest.

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