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Ab initio study of phase stability, lattice dynamics and thermodynamic properties of magnesium chalcogenides

Showkat H. Mir [a], Prakash C. Jha [b,*], Shweta Dabhi [c,d], Prafulla K. Jha [d]

[a] Centre for Nano Science, Central University of Gujarat, Gandhinagar 382030, India
[b] School of Chemical Sciences, Central University of Gujarat, Gandhinagar 382030, India
[c] Department of Physics, M. K. Bhavnagar University, Bhavnagar 364001, India
[d] Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara 390002, India

HIGHLIGHTS

- Van der walls dispersive forces are found useful in predicting the structural and mechanical properties of ionic solids.
- Very minute energy differences between B3 and B4 phases of magnesium chalcogenides were observed.
- The three considered phases (B1, B3 and B4) of magnesium chalcogenides are found dynamically stable at ambient conditions.
- Heat capacity and entropy are found to decrease with decrease in anion mass.

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ABSTRACT

The present work reports a comprehensive study of structural, dielectric, lattice dynamic and thermodynamic properties of magnesium chalcogenides MgX (X = S, Se, and Te) in rock-salt, zinc-blende and wurtzite crystal structures. Density functional theory calculations were performed using Perdew-Burke-Ernzerhof (PBE) functional (hereafter, PBE) and along with van der Walls interactions (hereafter, DFT-D). Our calculations show that the inclusion of van der Walls interactions improves the results and predict structural parameters close to the experimental values than using PBE functional alone. Both approaches show that the rock-salt phase is the ground state stable phase of MgS. The DFT-D calculations indicate that rock-salt whereas PBE results show wurtzite as the stable crystal structure for MgSe and MgTe respectively. Further, density functional perturbation theory has been employed to obtain the phonon dispersion curves and phonon density of states. The present phonon calculations show that these compounds are dynamically stable in the three considered phases. Thereafter, temperature dependent heat capacity at constant volume and entropy are also presented and discussed.

1. Introduction

The alkaline earth chalcogenides (AECs) are scientifically and technologically important materials due to versatility in their physical properties. AECs are important group of classical insulators with wide band gap ($E_g = 7–10$ eV) besides they also exhibit semiconducting properties with large valence bandwidth ($E_g > 6$ eV) [1]. These properties make them useful for numerous applications such as catalysis, microelectronics and luminescent devices [2–4]. Among the AECs, magnesium chalcogenides have recently engrossed much interest due to their potential applications in catalysis, optical and electrical devices [2–5]. Earlier studies have revealed that the magnesium chalcogenides can be used in high temperature and high power blue and ultraviolet wavelength optics [6–9]. For carrier confinement in alloys of II–VI quantum structures MgS can be used as an excellent barrier material [2,10,11]. MgSe is used in ZnSe based laser diodes and light emitting diodes (LEDs) as a cladding material [9]. Furthermore, magnesium chalcogenides are also an active choice for protective coatings due to their hardness, high melting point, high thermal conductivity and large bulk modulus [12]. These compounds are believed to exist in several crystallographic phases such as rock-salt (B1), zinc-blende (B3), wurtzite (B4), NiAs (B8) and FeSi (B28). However, there are still controversies

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[*] Corresponding author.
E-mail address: prakash.jha@cug.ac.in (P.C. Jha).

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and ambiguity about their ground state structure and high pressure phases due to very small energy differences among various structural phases.

In recent years, many research groups have reported the experimental [6,13–21] and theoretical [2–12,22–29] studies of magnesium chalcogenides MgX (X = S, Se and Te). From energy dispersive x-ray diffraction (EDXD) measurements under ambient pressure Peiris et al. [13] and Rouf et al. [14] have respectively shown that B1 phase is the ground state for MgS and MgSe. However, from epitaxial growth over GaAs substrate these materials were found to be stable in B3 phase [6,15]. It is also reported that MgSe undergoes a structural phase transition from B1 to B28 at about 99 GPa and approaches to sevenfold coordination at 202 GPa [14]. Mittendorf observed that the most stable phase of MgSe and MgS is wurtzite by evaporation of thin films through electron bombardment and annealing [16]. Several experiments have shown that B4 phase is the ground state structure for MgTe [17–21]. On the other hand, theoretical calculation performed through Hartree-Fock method and density functional theory (DFT) calculations within the generalized gradient approximation (GGA) indicate that B4 is the most stable phase for MgSe at ambient conditions [9,22,23]. Though, the DFT calculations using local density approximation (LDA) approach showed that the ground state structure for MgS and MgSe is B1 phase [8,9,23,24]. Camp et al. [25] reported six different phases for MgS and MgTe by employing LDA scheme and concluded that B1 is the ground state of MgSe whereas B8 is the ground state structure of MgTe. Li et al. [26] investigated the high pressure phase of MgTe and found a structural phase transition for MgTe from B4 to B8 phase in the pressure range of 1–3.5 GPa. Chaudhuri et al. [27] examined the high pressure properties of MgTe using LDA and proposed a phase transition around 190 GPa from B8 to PH_4I structure. Li et al. [28] have reported B8 and B31 (orthorhombic pnma) phases of MgTe from *ab initio* phonon calculations and predicted a phase transition from B8 to B31 around 42 GPa. Gökoğlu et al. [23] investigated the ground state of magnesium chalcogenides in five different phases using both LDA and GGA functionals and suggested a phase transition from B4 to B8 phase for MgTe at 1.1 GPa. Further, theoretical [8,23,29] and experimental [30–32] studies have been reported on the lattice vibrational (phonon) properties of MgX [8,23,29–32]. It is well known that many physical properties of solids such as specific heat, thermal expansion, heat conduction and electron–phonon interactions depend on the phonon dispersion. Besides, phonons also play an important role in understanding the dynamical stability of solids in a given structure.

Although, a number of studies have been performed for MgX, the effect of van der Walls interactions has not been investigated for these compounds despite its importance realized in ionic solids and layered structures. Moreover, the thermodynamic properties of MgX are not studied in detail as these are essential to understand the specific behaviour of a material. The MgX has been observed in many crystallographic phases such as B1, B3, B4, B8, B28 and PH_4I at different pressures, among them B1, B3 and B4 have been found to be stable in the vicinity of atmospheric pressure and the remaining phases exist in high pressure regime only. Thus, in the present work, we performed the comparative study of the ground state properties of magnesium chalcogenides in B1, B3 and B4 phases using density functional theory within the framework of PBE functional independently and PBE plus van der Walls (dispersive) forces. Thereafter, density functional perturbation theory (DFPT) is employed to calculate the phonon dispersion in the entire Brillouin zone [33–35] and subsequently the thermodynamic properties of these compounds are explored.

2. Computational methods

First, principle calculations were performed within the framework of DFT using plane wave pseudo-potential method implemented in quantum espresso code [36]. The exchange-correlation among electrons has been considered using GGA approximation within PBE functional [37]. Also, van der Walls interactions are found to be important for nanostructured and layered materials as well as for biological folding of macromolecules [38,39]. These interactions have also been found to significantly improve the structural and cohesive properties of bulk solids [39]. Therefore, besides using PBE functional, we also performed the dispersion corrected (DFT-D; where $E_{DFT\text{-}D} = E_{DFT} + E_{disp}$) method to investigate the structural and mechanical properties of magnesium chalcogenide. In DFT-D approach the dispersion energy was calculated by utilising equation (1) in which the damping function f_{damp} is included to turn-off the dispersive forces at short inter-nuclear distances [38].

$$E_{disp} = -\frac{1}{2} C_{6ij} \Big[\sum_{\vec{R}} |\vec{r}_{ij} + \vec{R}|^{-6} f_{damp}(\vec{r}_{ij} + \vec{R}) \Big] \tag{1}$$

$$f_{damp}(|\vec{r}_{ij} + \vec{R}|) = s_6 \left\{ 1 + \exp\left[-d \cdot \left(\frac{(|\vec{r}_{ij} + \vec{R}|)}{r_o} - 1 \right) \right] \right\}^{-1} \tag{2}$$

where s_6 is functional dependent scaling parameter, $\vec{R}$ are lattice vectors, $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ is the vectorial inter-atomic distance, the parameter d is used to tune the steepness of damping function, $\vec{r}_o = \vec{r}_{oi} - \vec{r}_{oj}$ is the sum of van der Walls radii of atom pairs. The C_{6ij} are semi-empirical parameters which are proportional to ionization energies and atomic polarizabilities which for each atom pair are computed using geometric mean of atomic terms.

A set of calculations were performed to converge the kinetic energy cut-off and k-point grid. Wave functions were expanded in a plane wave basis set with kinetic energy cut-off of 90 Ry (Rydberg) for MgS, MgSe, and 100 Ry for MgTe. A cut-off equivalent to 10 times to the energy-cut was employed for charge density in all calculations. For integration in Brillouin zone, we employed Monkhrost-Pack [40] k-mesh of 9 × 9 × 9 for MgS and MgSe while a k-grid of 10 × 10 × 10 is employed for MgTe. The Kohn–Sham equations were solved using conjugate gradient algorithm to find the total energy with convergence threshold of 1.0×10^{-6} Ry.

Phonon dispersion curves were obtained using density functional perturbation theory (DFPT) in the linear response approach [41,42]. This method avoids using supercell approach and allows the calculation of dynamical matrix at arbitrary q-points. Dynamical matrices were obtained at 8 × 8 × 8 and 6 × 6 × 4 q-point grids for cubic (B1 and B3) and hexagonal (B4) phases respectively. Thereafter, to calculate thermodynamic properties, we employed quasi-harmonic approximation (QHA) [43,44].

3. Results and discussions

The ground state of MgX (X = S, Se, and Te) is determined by calculating the total energy and enthalpy as a function of volume and pressure respectively for B1, B3 and B4 phases. The structural phase stability of a crystal is determined by Gibbs energy ($G = E + PV - TS$). Since the theoretical calculations are performed at 0 K, so the contribution from entropy is essentially negligible which reduces the Gibbs energy to enthalpy as ($G = E + PV$). Therefore, at a given pressure, the ground state is one which has the lowest enthalpy and a structural phase transition occurs when the