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First principles study of Mg_2X (X=Si, Ge, Sn, Pb): Elastic, optoelectronic and thermoelectric properties

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ABSTRACT

Full potential linearized augmented plane wave method within the framework of density functional theory was applied to calculate the structural, elastic, electronic, thermoelectric and optical properties of Mg_2X (X=Si, Ge, Sn, Pb) compounds. Exchange-correlation effects were treated using generalized gradient approximation and modified Becke–Johnson technique. Calculated structural parameters were found in good agreement to the experimental data. With the pressure application, the lattice constant decreased while the bulk modulus increased. Brittleness and ductility of these compounds were interpreted via the calculated elastic constants. The optical properties like complex dielectric function, refractive index, reflectivity, and optical conductivity were investigated in the pressure range 0–10 GPa. Very high reflectivity in a wide energy range indicates the usefulness of these materials as a shield from high energy radiations. In addition, the thermopower of the materials was calculated as a function of the chemical potential at various temperatures. These materials are suitable for applications in optoelectronic and thermoelectric devices due to their high thermopower and narrow bandgap.

1. Introduction

In recent years, magnesium based Mg_2X (X=Si, Ge, Sn, Pb) compounds have attracted attention due to their potential applications in optoelectronic, luminescent, and thermoelectric devices [1–15]. These compounds are also important owing to high thermal stability, low density, excellent compressibility, abundant availability, non-toxic nature, and low-cost [9]. They crystallize in face centered cubic antifluorite structure with space group Fm-3m (#225). Mg_2Si and Mg_2Ge are both semiconductors with an indirect band gap value of 0.66–0.78 eV for Mg_2Si and 0.57–0.74 eV for Mg_2Ge [10]. Mg_2Sn has a small band gap with a value of 0.36 eV [11], while the Mg_2Pb has a quite narrow indirect band gap of 0.028 eV [12].

Previously, the first-principle calculations based on the density functional theory (DFT) were performed to investigate the effect of hydrostatic pressure on the structural, electronic, and thermodynamic properties of Mg_2Sn [4]. The full potential linearized augmented plane wave (FP-LAPW) method within the local density approximation (LDA) was used to study the electronic and optical properties of Mg_2Si and Mg_2Ge under hydrostatic pressure [2]. The lattice dynamics and thermodynamic properties of Mg_2Si and Mg_2Ge were studied theoretically [1]. The electronic band structure and effective mass tensor of Mg_2Si were calculated, and spin orbit coupling effects on electronic properties was investigated [13]. Using the pseudopotential method within DFT structural, electronic, and mechanical properties of Mg_2Pb were investigated at high pressure [14]. However, no data have been reported on the pressure induced mechanical and optical properties for antifluorite Mg_2X (X=Si, Ge, Sn, Pb) have been reported [15]. Also the predicted results were underestimated than the available experimental results. Here, we have applied latest techniques to investigate properties of Mg_2X (X=Si, Ge, Sn, Pb). Also, we investigated and analyzed the pressure induced effect on the structural and mechanical properties for Mg_2X (X=Si, Ge, Sn, Pb). We have also calculated the thermopower as a function of the chemical potential of these antifluorite semiconductors at different temperatures. Furthermore, optical properties of these are also studied in a wide energy range.

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2. Methodology

Ab-initio calculations were performed using FP-LAPW method [16], which is known to be a precise and efficient approach to solve the Kohn–Sham equation within a framework of the DFT, as implemented in WIEN2K package [17]. We have employed Wu and Cohen generalized gradient approximation (WC-GGA) [18], which is based on exchange-correlation energy optimization to calculate the total energy. In addition, the recent Tran and Blaha-modified Becke–Johnson potential (TB-mBJ) [19] was also used for the electronic properties to avoid well-known GGA underestimation of the band gap. Following this method the unit cell is divided into non overlapping atomic spheres and interstitial regions. Inside the sphere, maximal value of l for wave function was expanded to $l_{\max}=10$ and was spherically symmetric while outside the sphere is constant. The parameters for secular matrix determination set $R_{MT}{}^{*}K_{\max}=7$. Where R_{MT} is used for Muffin-tin sphere radii and $K_{\max}$ is for cut-off wave vector in the first Brillouin zone. We have applied a 1000 k-point mesh in the whole Brillouin zone.

3. Results and discussion

3.1. Structural properties

Ground state volume optimization of the four anti-fluorite compounds was performed using an energy minimization procedure. The optimized ground state lattice parameters and bulk moduli are listed in Table 1, together with the available experimental and other computational data for comparison. Our calculated structural parameters show much closer agreement to the experimental parameters compared to other calculations [20]. It is noted from the table that the lattice constant increases while bulk moduli decreases by changing the cations X from Si to Pb in Mg_2X. This variation is due to the increasing ionic radii of X from Si to Pb. Furthermore, we have calculated the pressure variation of unit cell's lattice parameter and plotted in Fig. 1. It can be noted that the volume decreases uniformly with increasing pressure. The variation of the bulk moduli (calculated from the Charpin method [17]) versus pressure (Fig. 2) of the four compounds shows monotonic increase with pressure as is expected from the pressure versus lattice constant's plot.

Table 1
Calculated lattice constants and bulk moduli of Mg_2X (X=Si, Ge, Sn, Pb). Experimental and previous theoretical data are also quoted for comparison.

Compounds	Properties	This work	Experiments	Calculations
Mg_2Si	a (Å)	6.33	6.338[a], 6.35[b]	6.26[c], 6.295[d], 6.3[e]
	B (GPa)	58.5	59[f]	58.84[c], 56.2[d]
Mg_2Ge	a (Å)	6.37	6.393[a]	6.29[c], 6.12[g], 6.318[d], 6.35[e]
	B (GPa)	54	44.0–54.7[f]	56.12[c], 57.6[g], 55.1[d]
Mg_2Sn	a (Å)	6.73	6.765[h], 6.759[f]	6.52[g], 6.99[e]
	B (GPa)	42	41.2[i]	42.9–41.9[g]
Mg_2Pb	a (Å)	6.83		5.495[f], 6.92[e]
	B (GPa)	41		38.6[i]

Ref. [25].

[a] Ref. [21].
[b] Ref. [22].
[c] Ref. [2].
[d] Ref. [24].
[e] Ref. [20].
[f] Ref. [26].
[g] Ref. [23].
[h] Ref. [12].
[i] Ref. [15].

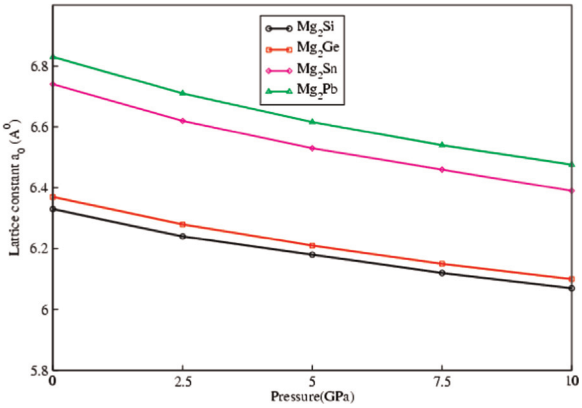

Fig. 1. Pressure induced variation in lattice parameters for Mg_2X (X=Si, Ge, Sn, Pb).

3.2. Elastic properties

The elastic stiffness constants for a cubic crystal can be reduced to three independent coefficients C_{11}, C_{12} and C_{14} by virtue of cubic symmetry. Elastic stiffness constants are calculated by applying small strain to the equilibrium unit cell and determining the corresponding variations in the total energy. The elastic constants C_{ij} are obtained by using Charpin method implemented in Wien2K code [17]. The first equation involves calculating the bulk modulus B, which is related to the elastic constants by the following relation;

$$B=\frac{1}{3}(C_{11}+2C_{12}) \tag{1}$$

The second one involves applying volume-conserving tetragonal strain

$$\vec{\varepsilon}=\begin{pmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & 0 \\ 0 & 0 & \dfrac{1}{1+\varepsilon^2}-1 \end{pmatrix} \tag{2}$$

Application of this strain changes the total energy from its initial value as follows:

$$E(\varepsilon)=(C_{11}-C_{12})6V_0\varepsilon^2+O\left(\varepsilon^3\right) \tag{3}$$

where V_0 is the volume of the unit cell.

Finally, for the last type of deformation, we used the volume-conserving rhombohedral strain tensor given by

$$\vec{\varepsilon}=\frac{\varepsilon}{3}\begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \tag{4}$$

which transform the total energy to

$$E(\varepsilon)=\frac{V_0}{3}(C_{11}+2C_{12}+4C_{44})\varepsilon^2+O\left(\varepsilon^3\right) \tag{5}$$

These three equations form the set of equations needed to determine the full elastic tensor. The calculated values of C_{11}, C_{12} and C_{44} for Mg_2Si, Mg_2Pb Mg_2Sn and Mg_2Ge are shown in Table 2 along with other calculated and experimental values. Our calculated elastic constants are generally improved than the previous theoretical results compared to the experimental data. In view of Table 2, the calculated C_{11} value, which is related to the unidirectional compression along the principal crystallographic directions, is much higher than that of C_{44}, which represents the resistance to