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Ab-Initio Study of Electronic and Optical Properties of the Mg2X (X= Si, Ge, Sn)

Uma Shankar Sharma
Nano Material Lab, RJIT BSF Academy Tekanpur, Gwalior, MP-475005, India
Corresponding Author: Uma Shankar Sharma

Abstract : *The present work is the investigation of the electronic and optical properties of chalcopyrite materials using ab-initio methods based on Density Functional Theory (DFT) using pseudo potential method implemented in SIESTA computational package. For the exchange-correlation potential, the local density approximation (LDA) and generalized gradient approximation (GGA) were used to calculate the lattice parameters, Bulk modulus and its first derivative as well as the densities of states, partial density of state and optical properties of the semi metallic semiconductors materials based on Mg_2X (X=Si, Ge and Sn). The achieved results were compared to computational works and other data acquired experimentally. The band gap of Mg_2Si, Mg_2Ge and Mg_2Sn indirect in nature. The valence band and conduction band near Fermi level are mainly contributed from X 6p state and Mg 2p states respectively. The optical properties of Mg_2Si, Mg_2Ge and Mg_2Sn are isotropic characteristics, the refractive index Mg_2Si, Mg_2Ge and Mg_2Sn are 4.02, 1.01 and 1.01 respectively. It is clear that as ionic radii increase structural and electronic properties of these compound changes accordingly. This analysis result indicates that the frequency area of 1.187–3.25 eV is the strongest absorption zone which is infrared to the visible region of electromagnetic radiations for Mg_2Si.*

Keywords - *DFT, optical properties, Mg_2X*

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I. Introduction

Magnesium silicides, germanide, stannide (Mg_2X, X= Si, Ge, Sn) are narrow bandgap material crystallizes in a face-centered cubic (fcc) structure. The structure symmetry of the Mg_2X corresponding space group is $Fm\bar{3}m$ (group number 225) belongs to the antifluorite structure family have attracted the attention in the last years[1]. Among them, Silicides are attractive thermoelectric materials because they are based on cheap, abundant, and nontoxic elements. Recently, Mg_2X (X=Si, Ge, Sn) compounds have shown the development of alloy conductor materials, which is due to its abundant raw availability and excellent thermal effect, especially its excellent thermoelectric characteristics. Such - Mg_2X metal compound crystals have the features of resistance to corrosion, withstanding high temperatures, high electrical conductivity and low thermal conductivity, etc. [2]. Thereby Mg_2X based thermoelectric materials have gained wide attention from researchers and have been referred to as a new type of semiconductor material environment [3-5].

Theoretical study of phase transition, mechanical and thermodynamic properties of magnesium alloy have been studied [6,7] and literature [8] revealed that it can effectively optimize the crystal structure and enhance the mechanical properties through adding another element to magnesium alloys. Since electronic structure plays a key role in semiconductor optoelectronic properties. Therefore, the calculations of the band structure of Mg_2X compound become a topic of great interest in the field of computational materials.

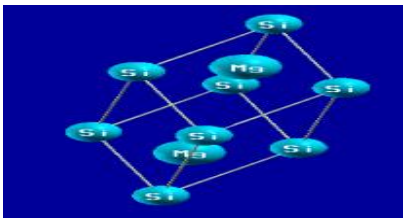
The elastic properties at different temperatures studied by Ganeshan[9] and Buchenauer et al [10,11] further calculated the electronic and optical properties of Mg_2Sn and obtained its elastic constants and transverse optical wave frequency.

In the present, study the structural properties (lattices parameters, bulk modulus and its first derivative), the electronic properties (total and partial density of states) and optical properties (real and imaginary part of the refractive index, conductivity, refractive index) for Mg_2X(X=Ge, Si, Sn) compounds.

II. Computational Details

In the present calculation, the investigations are accomplished by employing pseudo potential method framed within density functional theory DFT as implemented in SIESTA code[12]. Density-Functional Theory (DFT) approach[13,14] has been used throughout this work at the generalized gradient approximation (GGA). The Perdew-Becke-Ernzerhof (PBE) exchange and correlation functional was used[15,16]. Norm-conserving pseudo potential based on the Troullier-Martins scheme was utilised to model core electrons. We have carried out convergence tests of total energy Etot for Mg_2X (X=Ge, Si, Sn) as the function of lattice constant and plane

wave cut off (K-points) over reduced Brillouin zone. The calculations were performed in a self-consistent way, using the two approximations mentioned below. The integration over the Brillouin zone was performed on a grid of k-points. The corresponding set of k-points were calculated using the Monkhorst-Pack scheme [17]. The quality of the kinetic energy cutoff and a grid of k-points were tested on the calculated cell parameters constants of the Mg_2Xstructure.



Mg_2Si Structure

Mg_2X crystallizes in a face centered cubic (fcc) Bravais lattice with primitive translation vectors a = *a*(0, 0.5, 0.5), b = *a*(0.5, 0, 0.5) and c = *a*(0, 0.5, 0.5) where *a* is the lattice parameter. The structure symmetry of Mg_2X corresponding space group $Fm\bar{3}m$, in which three in-equivalent sites can be specified in the irreducible unit cell, namely Si: *a*(0, 0, 0), Mg: *a*(0.25, 0.25, 0.25), and Mg:: *a*(0.75, 0.75, 0.75).

Results And Discussion

Structural properties for Mg_2X (X= Ge, Si, Sn)

The lattice equilibrium parameters determine to plot total energy varies as the function of those parameters and realize structural optimization on Mg_2X as shown in fig1 and parameter are shown in table 1. The minimization of total energy was achieved by computing total energy for different lattice parameters around experimental value.

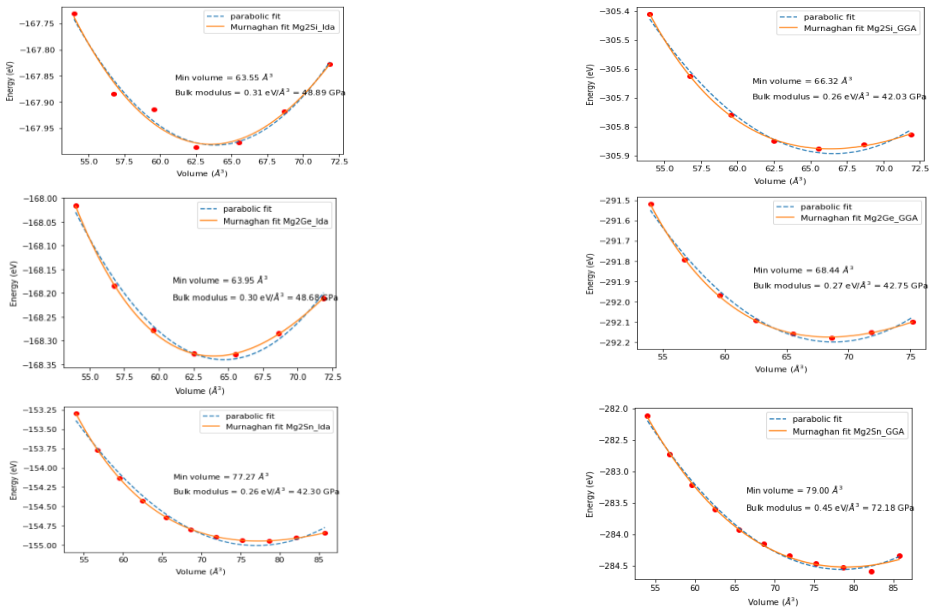


Figure 1. The total energy variation as function of volume for Mg2X

Table 1: Structural parameters of Mg_2X

Parameter	Mg_2Si				Mg_2Ge		Mg_2Sn	
	GGA	other	LDA	other	GGA	LDA	GGA	LDA
a(A)	6.64	6.42[18]	6.634	6.28[19]	6.493	6.34	6.83	6.76
V(A)	66.32		63.55		68.44	63.93	82.22	77.27
B0 (GPa)	42.02	49.75[18]	48.89	56.08[19]	42.75	48.68	48.68	42.30
B'_0	4.32	4.29[18]	4.53	4.48[19]				

he equilibrium volumes for all the investigated compounds were obtained by fitting the total energy as the function of Murnaghan's equation state [4]. In which B_0 and B'_0 are respectively the equilibrium bulk modulus and its first derivative of pressure and V_0 being the equilibrium unit cell volume. The lattice parameter corresponding the ground state is obtained from the minimum of Etot(eV).

Electronic properties

The band structure, total density of states and partial density of states for Mg_2X(X= Si, Ge, Sn) are shown in figure 2. The valance band maxima at point and conduction band minimum at X point which indicates that the Mg_2X are indirect narrow band gap semiconductor. The bandgap calculated from DFT are underestimated to the experimental result due to the poor description of exited states in which the polarization effect is not accounted by the exchange-correlation function[20].

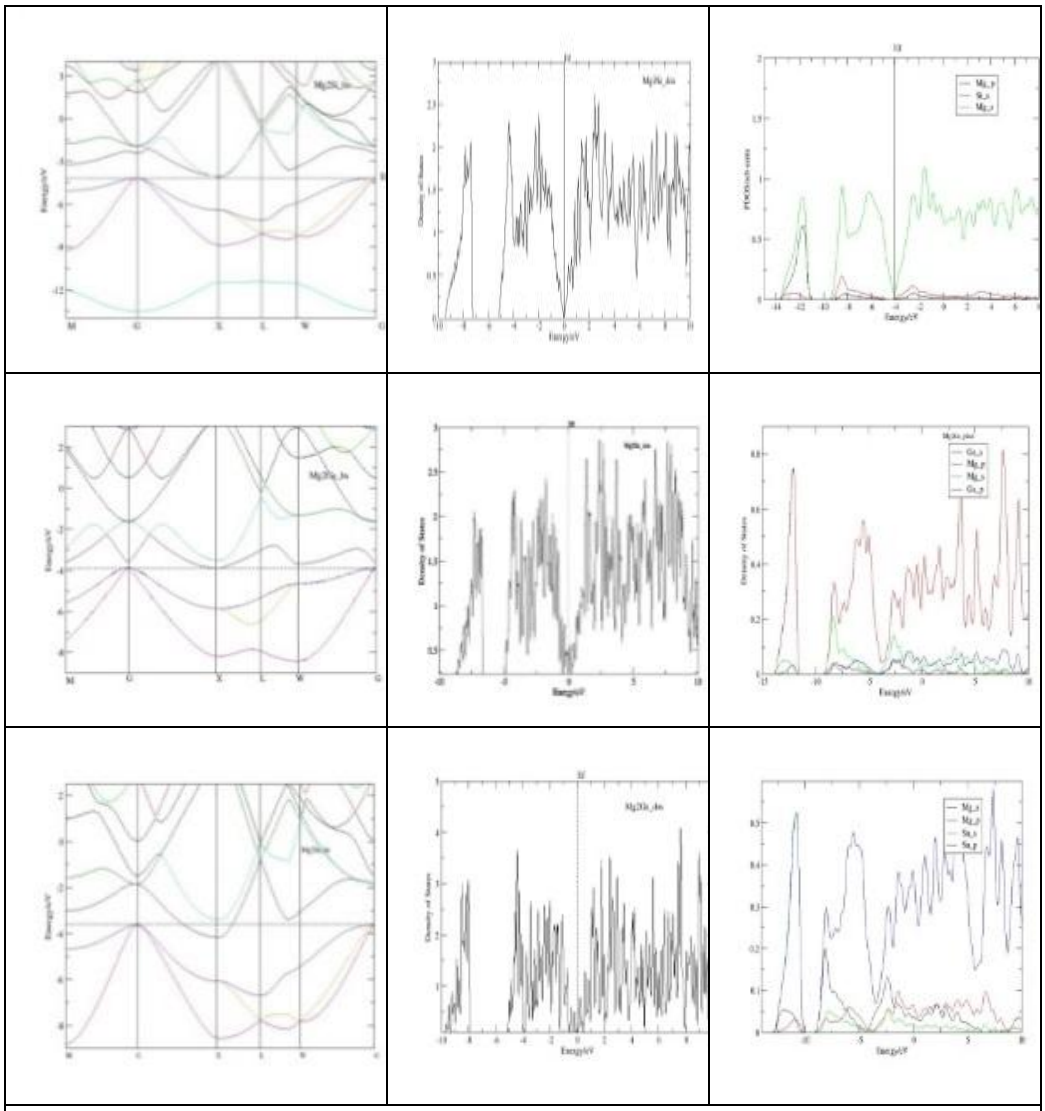


Figure 2: (a)Band Structure (b) Density of states and (c) Partial Desnsity of States of Mg_2X

It is also clear from figure that the below Fermi level, the bands near -9 eV are due to the *p*-states of X(=Ge, Si, Sn) and above the Fermi level is due to the hybridization of *d*-state of Mg and small contribution of *p* or *d*-states of X(=Ge, Si, Sn).

We can deduce that Mg_2X compounds have semiconducting character according to the density of states (DOS) and the individual contribution of different orbitals in the partial density of states (PDOS). The valence band is divided into two bands; the lower one is dominated by s orbital of X(=Ge, Si, Sn) with no neglected contribution of Mg-3*s* and Mg-3*p* orbitals. The second is between (-9 and -4eV) for Mg_2X and Mg_2Sn, between (-10and -8ev) for Mg2Ge below Ef, is dominated by Ge-4*s*, Si-3*s* and Sn-5*s* contribution.

According to our decomposition of total and partial densities, we have shown that the valence electrons are

mainly around the X (=Si, Ge, Sn). Although, there is a weak covalence between Mg and the X. The DOS of Mg2Si indicate that the mobility of carriers is larger than transition metal silicides [20]. The similar trend also found in Mg2Ge and Me2Sn compound that the *s*, *p* states of Mg hybridized mutually in the DOS near the Fermi level which lead to enhance the mobility of charge carriers and conductivity in Mg_2X compounds that prove their semimetal behaviour.

Optical properties

The optical properties of solids are based on the band structure, the nature of the basic peaks in theoptical spectrum be interpreted in terms of the interband transitions responsible for the peaks. The spectral profiles are indeed very similar to each other. Here in the present study a brief account mainly focusing on the location of the interband optical transitions. Fig 3(a) is the calculated curve of refractive index versus photon energy in electron volt of Mg_2X belongs to the anti-fluorite structure and optical properties possess isotropic.

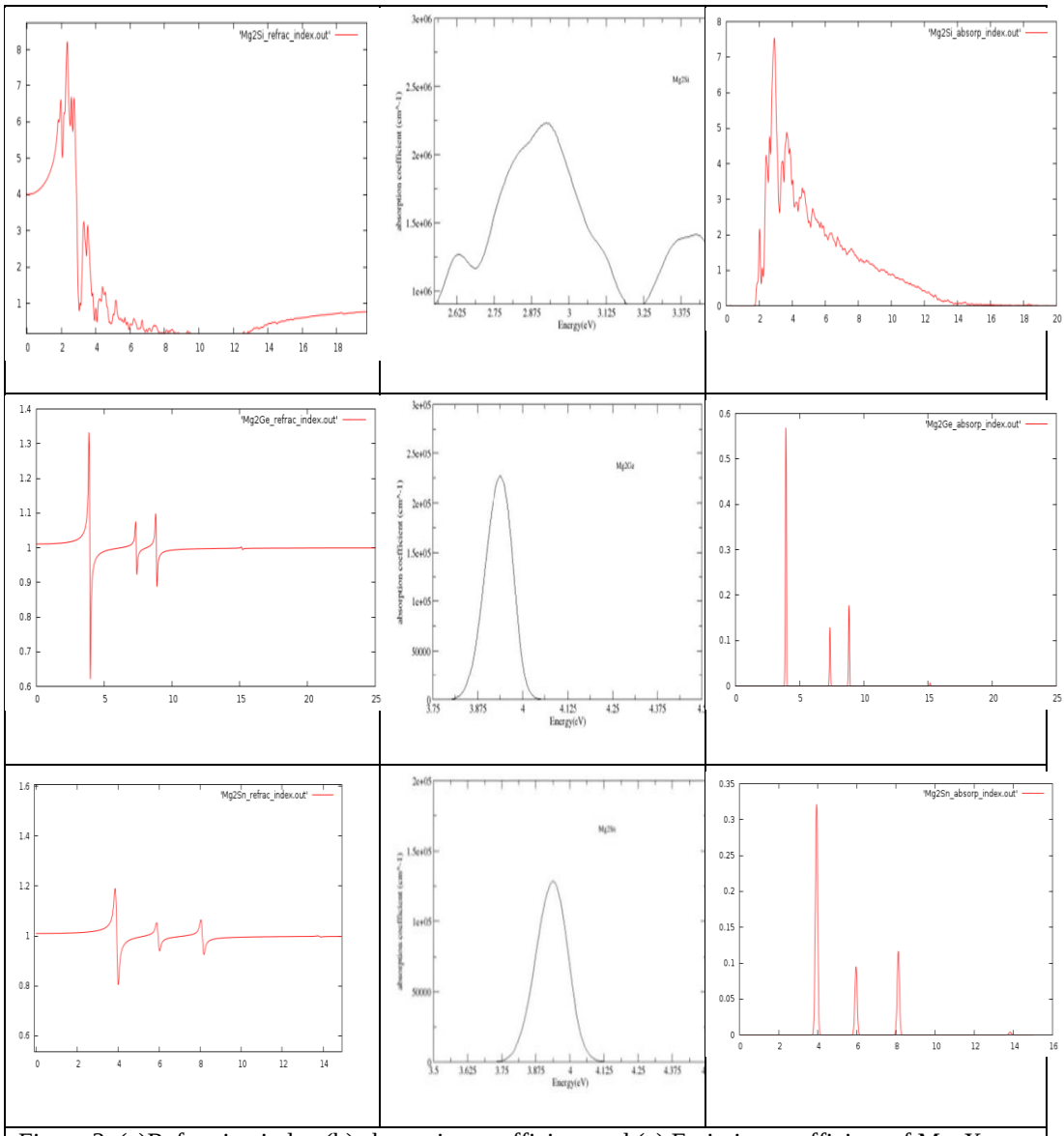


Figure 3: (a)Refractive index (b) absorption coefficient and (c) Extintion coefficient of Mg_2X

The peak structures in Figs.3 can be explained from the band structure discussed above. The refractive index of Mg_2Si is higher than Mg_2Ge and Mg_2Sn. The refractive index of Mg_2Si is 4.02 which slightly less than 4.34 [20]. Figure 3(b) shows the absorption coefficient of Mg_2X. In the photon energy range of 0–4.5eV, the absorption coefficient of Mg_2Si reaches the maximum first peak of 2.24×10^6 cm^{-1} in the photon energy of 2.937eV, whereas the absorption coefficient of Mg_2Ge and Mg_2Sn reaches the maximum peak of 1.25×10^5 cm^{-1}

and 2.75×10^5 cm^{-1}respectively. The absorption coefficient of Mg2Si decreased to zero in the photon energy range of 1.187–3.25 eV indicates Mg_2Si should be colourless and transparent. In the photon energy range of 1.187–3.25 eV, the absorption coefficient of Mg_2Si reaches the second peak of 1.75×10^6 cm^{-1} in the photon energy of 3.435eV. This analysis result indicates that the frequency area of 1.1875–3.25 eV is the strongest absorption zone which is infrared to the visible region of electromagnetic radiations for Mg_2Si.

III. Conclusion

To conclude, the electronic and optical properties of the Mg_2X compound were calculated by using ab-initio methods based on Density Functional Theory (DFT). The result shows the indirect band gap of Mg_2X (X=Si, Ge and Sn) compound. The lattice constant 6.425, 6.439 and 6.83 ang of Mg_2Si, Mg_2Ge and Mg_2Sn respectively whereas bulk modulus 42.03, 42.75 and 48.68 GPa. The band gap of Mg_2Si, Mg_2Ge and Mg_2Sn are indirect in nature. The valence band and conduction band near Fermi level are mainly contributed from X 6*p* state and Mg 2*p* states respectively. The optical properties of Mg_2Si, Mg_2Ge and Mg_2Sn are isotropic characteristics, the refractive index Mg_2Si, Mg_2Ge and Mg_2Sn are 4.02, 1.01 and 1.01 respectively. It is clear that as ionic radii increase structural and electronic properties of these compound changes accordingly. This analysis result indicates that the frequency area of 1.1875–3.25 eV is the strongest absorption zone which is infrared to the visible region of electromagnetic radiations for Mg_2Si.

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