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First-principles study of phase transition, electronic, elastic and optical properties of defect chalcopyrite $ZnGa_2Te_4$ semiconductor under different pressures

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ABSTRACT

The generalized gradient approximation (GGA) within the framework of density functional theory (DFT) has been used to investigate the phase transition, electronic, elastic and optical properties of $ZnGa_2Te_4$ defect chalcopyrite (DC) semiconductor at different pressures. At 18 GPa pressure, $ZnGa_2Te_4$ semiconductor has been found to undergo a structural phase transition from defect chalcopyrite (DC) to disordered rocksalt (DR) structure (phase). The calculated bandgap of DC structure at ambient pressure has been found to be 0.95 eV with direct in nature. The band structure of DR phase studied at 18 GPa pressure has been discussed through density of states. Pressure-dependent elastic stiffness coefficients (C_{ij}), bulk modulus (B), shear modulus (G), Young modulus (E), Poisson's ratio (σ), B/G ratio and Zener anisotropy factor (A) have been calculated at 0, 10, 18 GPa pressures for DC phase and at 20, 25, 30 GPa pressures for DR phases. Further, optical properties such as dielectric function, refractive index, extinction coefficient, absorption coefficient, reflectivity and loss function have been estimated at 0, 10 and 18 GPa pressures for DC phase. The calculated parameters have been compared with the available experimental and theoretical values. A fairly good agreement has been obtained between them.

1. Introduction

Defect chalcopyrite (DC) semiconductors crystallize in tetragonal structure with chemical formula AB_2X_4 (A = Zn, Cd, Hg; B = Ga, Al; X = S, Se, Te) nearly the subgroup of chalcopyrite materials at ambient condition attract much attention in the research community because of their excellent electronic, elastic, optical and nonlinear properties [1,2]. The defect chalcopyrite semiconductors are of greatest technological interest and have potential applications in the fields of photovoltaic devices, photo-detector and nonlinear optics [3,4]. These semiconductors have also been used for solid-state lasers such as optical parametric oscillators (OPOs) and frequency doubling devices due to their high laser damage threshold values and conversion efficiency [5,6]. Further, presence of strong anisotropy and lack of cubic symmetry make these compounds optically birefringent and therefore, suitable for phase matching applications. Various experimental and theoretical studies have been carried out to understand different properties of defect chalcopyrite (DC) semiconductors [7–24]. The first principle calculations of $CdGa_2X_4$ (X = S, Se) [7], XAl_2Se_4 (X = Zn, Cd, Hg) [8–12], $ZnIn_2Te_4$ [13,14] and $ZnGa_2Te_4$ [15,16] have been performed to investigate the structural, electronic, optical and nonlinear properties. Jiang and Lambrecht [17] have studied the electronic band structure of DC semiconductors and correlated them with their parent chalcopyrite materials. Theoretically, the variation of structural and electronic properties of $CdAl_2Se_4$ has been calculated under different temperature and pressure [18]. The spectroscopic-ellipsometry (SE) and thermoreflectance (TR) spectra have been measured in the range 1.2–5.2 eV and 1.0–6.0 eV, respectively, for $CdIn_2Te_4$ semiconductor by Take et al. [19]. The effects of temperature on lattice parameters and thermal expansion coefficients have been calculated employing X-ray powder diffraction measurement technique [20]. Hecht et al. and others [21,22] have studied the vibrational and electronic properties of CdA_2B_4 (A = Al, Ga and B = S, Se) semiconductors. The electrical conductivity and dielectric properties of $CdGa_2S_4$ thin film have been investigated by employing conventional thermal evaporation technique [23]. Experimentally, the optical properties of both amorphous and crystalline forms of $ZnIn_2Te_4$ have been determined by Ozaki et al. [24,25]. Razzetti et al. and co-researchers [26,27] have measured the

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directional dispersion of polar phonons in the defect chalcopyrite crystals using iodine as a transport agent.

Attempts have been made to understand the phase transition in defect chalcopyrite semiconductor under pressure. In particular, X-ray diffraction (XRD), Raman spectroscopy and optical absorption measurements have been performed on $ZnGa_2Se_4$ [28,29], $CdGa_2Se_4$ [30], $CdAl_2X_4$ (X = S, Se) [31,32] and $ZnGa_2Te_4$ [33] semiconductors at high pressure. Recently, the author has investigated the linear [34,35] and nonlinear properties [36,37] of chalcopyrite semiconductors. The Raman scattering spectroscopy under varied pressures has been employed to investigate the phase transitions and Raman modes [38–41]. Also, it has been observed, at ambient temperature and under high pressure, the DC materials undergo a structural phase transition from tetragonal to rocksalt structure [32,42]. Moreover, thiospinels have shown to undergo to a partially ordered rocksalt structure under pressure [43]. So far, no work has been carried out using density functional theory (DFT) considering the effect of pressure on electronic, elastic and optical properties of $ZnGa_2Te_4$ semiconductor. Moreover, literature survey shows that $ZnGa_2Te_4$ is less studied compared to other defect chalcopyrite semiconductors. So, it has been thought of interest to study various properties of this semiconductor under pressure. In this article, we have used generalized gradient approximation (GGA) within the framework of density functional theory (DFT) to investigate the stability, electronic, elastic and optical properties of both defect chalcopyrite and rocksalt structures at different pressures.

2. Computational details

The first principle calculations have been performed within the framework of density functional theory (DFT) [44] using Atomistic Toolkit-Virtual Nanolab (ATK-VNL) [45] based on local combination of atomic orbitals (LCAO) method. To describe exchange-correlation interaction of electrons, generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) parameterization has been used. In the present study, pseudo-atomic OMX basis sets [46,47] represent the wave functions considering 3 d and 4s states of Zn, 3 d, 4s and 4p states of Ga, and 3 d, 5s and 5p states of Te as valence states. It is well known that OMX basis sets also consider the semi-core states for accurate calculation. The Brillouin zone integration for defect chalcopyrite (DC) and disordered rocksalt (DR) phase have been performed using $8 \times 8 \times 5$ at and $13 \times 13 \times 13$ Monkhorst-Pack grid [48], respectively. The mesh cut-off of 300 Hartree (Ha) and 400 Hartree (Ha) have been used for the defect chalcopyrite (DC) and disordered rocksalt (DR) phase, respectively. For geometry optimization, limited-memory Broyden-Fletcher-Goldfarb-Shanno (LBFGS) [49] optimization technique has been employed wherein the atoms were allowed to relax under the criteria of force tolerance 0.01 eV/Å, stress tolerance 0.02 GPa and a total energy difference less than 1×10^{-8} Ha has been used for self-consistent calculations.

3. Results and discussion

3.1. Structural optimization and electronic properties

$ZnGa_2Te_4$ is a defect chalcopyrite (DC) semiconductor which crystallizes in body-centered tetragonal with space group $I\bar{4}$ (#82) with seven atoms per unit cell. In the conventional unit cell of DC-$ZnGa_2Te_4$, the atoms occupy Wyckoff positions Zn (0,0,0), Ga^1 (0, 0,0.5), Ga^2 (0,0.5,0.25) and Te (0.2752,0.234,0.1357) [33] as represented in Fig. 1(a). The high-pressure phase of $ZnGa_2Te_4$ structure has a disordered rocksalt (DR) structure with space group $Fm{-}3m$ (#225). The atomic positions for the DR phase are Zn (0,0,0), Ga (0,0,0) and Te (0.5,0.5,0.5) occupying a fractional occupancy of 0.25, 0.5, and 1, respectively [33] as shown in Fig. 1(b). The total energy vs volume curves for both phases at ambient pressure have been calculated and shown in Fig. 2.

The calculated lattice parameters of both structures are listed in Table 1 and found to be in good agreement with the experimental and theoretical values. Further, the bulk modulus (B) and its pressure derivatives (B') have been calculated for DC-$ZnGa_2Te_4$ and DR- $ZnGa_2Te_4$ using second and third-order Birch-Murnaghan equation of states (EOS). The calculated values of B and B' are also listed in Table 1 and compared with the available known values.

At T = 0 K and zero pressure, the energy versus volume curves of DC and DR phases of $ZnGa_2Te_4$ plotted in Fig. 2 shows that DC phase is more stable than the DR phase. In order to study the phase transition of $ZnGa_2Te_4$ from DC to DR structure and their structural phase stabilities, Gibbs free energies is calculated. The Gibbs free energy is defined as:

$$G = U + PV - TS \quad (1)$$

where U is the internal energy of the system, PV is the volume work, and TS is the vibrational energy.

In the present work, at T = 0 K, the enthalpies ($H = U + PV$) are calculated for the optimized DC and DR structures at pressures of 5, 10, 20 and 30 GPa. The point of intersection of the two enthalpy curves correspond to phase transition of $ZnGa_2Te_4$ semiconductor from DC to DR structure and is found to be 18 GPa as shown in Fig. 3. However, our calculated transition pressure overestimates the experimental value of 12.5 GPa [33]. This difference of 5.5 GPa from the experimental value is mainly due to the temperature difference and purity of the powder sample used in the experiment. Also, we have drawn an insert diagram in Fig. 3. It is found that change in enthalpy becomes negative for DR structure at 18 GPa pressure. Hence, the DR structure is more stable after 18 GPa pressure. However, before phase transition DC structure is stable.

Further, analysis of the structural phase transition from DC to DR structure was carried out by calculating the normalized cell volume (V/V_0), where V denotes the volume of the conventional unit cell at a particular pressure and V_0 denotes the equilibrium volume of the DC phase at zero pressure. The V/V_0 vs pressure curve is plotted in Fig. 4. It is found that the calculated volume collapse ($\Delta V/V_0$) at the phase transition pressure is 53.9% which is very close to the experimental value of 52.4% [33].

The band structures of the $ZnGa_2Te_4$ semiconductor have been investigated using the optimized structures of DC and DR phases. The calculated band structure of DC phase at 0 GPa is plotted in the energy range −14 eV to 10 eV as shown in Fig. 5(a). The Fermi level is set to zero. The calculated band gap of DC-$ZnGa_2Te_4$ semiconductor is found to be 0.95 eV and listed in Table 1. Our calculated band gap is in good agreement with the experimental values [3] and values reported by other workers [15–17]. Further, band structure of DR phase has been calculated at the transition pressure and shown in Fig. 5(b). From Fig. 5(b), it is clear that the valence band and the conduction band overlap with each other and shows metallic in nature.

To further analyze the electronic behavior of the DC and DR phases of $ZnGa_2Te_4$, the energy distribution of different electronic states can be visualized using partial density of states (PDOS) and total density of states (TDOS). Fig. 6(a) and (b), show the total density of states (TDOS) and partial density of states (PDOS) of DC and DR structure at 0 GPa and at 18 GPa pressures, respectively.

From Fig. 6(a), it can be observed that the valence band of DC-phase can be divided into three sub-bands i.e., lowermost, middle and uppermost band. The lowermost band from −11.91 eV to −10.32 eV in the TDOS plot is mainly due to the hybridization of Te-s, Ga-s and Zn-s/d states. The middle band from −6.86 eV to −6.7 eV is mainly contributed by Zn-d state. The uppermost valence band from −6.4 eV to the Fermi level is predominantly due to Te-p, Ga-s/p, and Zn-s/p/d states. The lower conduction band ranging from 0.95 eV to 3.12 eV is constituted by Zn-s, Ga-s/p and Te-p/d states while the upper portion starting from 3.12 eV till 10 eV is due to Ga-p/d, Te-p/d, and Zn-p states. In case of the DR-phase, PDOS and TDOS are plotted in Fig. 6(b) and it is observed that the valence and conduction bands overlap