Ab-initio investigations of electronic, optical, mechanical and thermal properties of Ca$_{0.875}$Ba$_{0.125}$Te

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Abstract. The ground-state properties and optical, mechanical, elastic and thermal properties of the Ca$_{0.875}$Ba$_{0.125}$Te alloy have been studied by using the full potential linearized augmented plane wave (FP-LAPW) scheme based on the density functional theory in the frame of generalized gradient approximation (GGA). In order to model Ca$_{1-x}$Ba$_x$Te alloy, 16-atoms supercell of the type 2 x 2 x 2 is employed. The lattice structure of Ca$_{0.875}$Ba$_{0.125}$Te alloy is obtained by replacing one Ca atom by one Ba atom in the crystal lattice of CaTe. The charge density plot, electronic structure and density of states plots are made and discussed for the alloy. The lower valence band maxima (VBM) and the upper conduction band minima (CBM) of Ca$_{0.875}$Ba$_{0.125}$Te alloy is located at Γ point, ensuing in a direct band gap, whereas in case of parent element CaTe the nature of the band gap is indirect. The characteristic properties of Ca$_{0.875}$Ba$_{0.125}$Te alloy is dominated by Te 5p electrons (below the Fermi level) and Ba 4d and Ca 3d electrons (above the Fermi level).

1. Introduction

Recently, the investigation of the II-VI semiconductor compounds has become an area of great activity. A lot of experimental reports and theoretical studies are available for II-VI chalcogenides such as calcium chalcogenides [1], strontium [2] and beryllium chalcogenides [3]. At ambient conditions, the alkaline metal earth chalcogenides crystallizing in the NaCl type structure [4,5]. Technologically, the rare earth chalcogenides are significant materials in the applications namely catalysis, microelectronics, luminescent devices [6,7], infrared sensitive devices [8,9], etc. The II-VI semiconductors and the semiconductor heterostructures are familiar to form ternary alloys with a direct energy band gap and high absorption coefficients [10]. The energy gap values of ternary II-VI semiconductors and its alloys include several light spectra and lattice parameters can be made independently to produce photovoltaic devices on appropriate substrate [11]. They are used as potential resources for making thin film heterojunction photo-voltaic devices.

Ca-based chalcogenides are more interesting due to their anion and cation radius ratio ensuing in high phase transition pressures. Many experimental and theoretical investigations have been made to explain the structural, electronic, elastic, optical and thermo dynamical properties. The structural change and pressure volume relationships in CaTe and SrTe at high pressure are investigated by Zimmer et al. [12]. Cohesive property of CaX compounds under pressure reported by Cartona et al. [13]. The elastic properties are studied by using pseudo potential [14] and tight binding theory [15]. Structural and elastic
properties at high pressure have been investigated by Arya et al. [16]. By using FP-LAPW scheme, the optical properties of Ca-based chalcogenides have been reported [17]. Ab initio investigations of calcium chalcogenides are made by Slimani et al. [18]. Here, the focus is made on investigation of the ground state properties and elastic, mechanical and optical properties of barium doped CaTe semiconductor. It has been found that the phase transition from NaCl-type structure to CsCl-type structure in ternary Ca$_{0.875}$Ba$_{0.125}$Te. The most important characteristics of the absorber material in a solar cell are direct band gap in the range of 1.0 -1.7eV and high absorption coefficient. The parent binary CaTe alloy has indirect band gap and its energy gap value is 1.587 eV, whereas the Ba doped CaTe (ternary Ca$_{0.875}$Ba$_{0.125}$Te) alloy has direct band gap and its energy gap value 1.647 eV is close to the optical energy gap of solar cell absorbers. Hence, from this study it has been identified that the ternary Ca$_{0.875}$Ba$_{0.125}$Te is suitable for solar cell absorber. Further, the electrical, mechanical and optical properties of Ca$_{0.875}$Ba$_{0.125}$Te alloy has been discussed in the present study.

2. Method of Calculations

FP-LAPW method is employed to calculate the structural properties, electronic, mechanical, elastic and optical properties of CaTe and Ca$_{0.875}$Ba$_{0.125}$Te alloys. All the calculations are carried out by the Wien2k code [19] within the frame of DFT. The generalized gradient approximation (GGA) as parameterized by Perdew, Burke and Ernzerhof (PBE) [20] is employed for the exchange-correlation potentials. The value of $l_{\text{max}}$ for the wave function expansions inside sphere is confined to $l_{\text{max}} = 10$. The $R_{\text{MT}}$ x $K_{\text{max}} = 7$ and $G_{\text{max}} = 12$ is selected for the plane wave expansions in interstitial region and charge density Fourier expansion respectively. The $R_{\text{MT}}$ (muffin-tin radius) was assumed to be 2.5 for Ca, 2.5 for Ba and 2.08 for Te atoms. For k-space summation the 10 x 10 x 10 k-points have been used. Self-consistent calculations are repeated up to the total energy converges to less than 0.0001Ry and charge converge to less than 0.001eV. To model the Ca$_{0.875}$Ba$_{0.125}$Te alloy, we employ a 16-toms supercell of the type 2 x 2 x 2 and the lattice structure of Ca$_{0.875}$Ba$_{0.125}$Te is obtained by replacing one Ca atom with an equal number of Ba atom in the crystal lattice of CaTe.

3. Result and Discussions

3.1. Structural properties

Structural properties of CaTe and its ternary alloy Ca$_{0.875}$Ba$_{0.125}$Te investigated at ambient condition by using GGA scheme. CaTe crystallizes in NaCl-type B1 structure (space group 225) and Ca$_{0.875}$Ba$_{0.125}$Te crystallizes in CsCl-type B2 structure (space group 221). 

The position of Ca and Te atom is situated at (0,0,0) and (0.5,0.5,0.5) respectively. The ternary Ca$_{0.875}$Ba$_{0.125}$Te is found to undergo a phase transformation from NaCl-type (Fm3m) to CsCl-type (Pm3m) structure. The lattice constant $a_0$, bulk modulus B and B’ (pressure derivative bulk modulus) values are obtained by fitting the energy versus volume according to Birch-Murnaghan’s equation [21].

The calculated structural properties of CaTe and Ca$_{0.875}$Ba$_{0.125}$Te alloys are presented in Table 1. All the calculated results of the parent compound CaTe are well matched with the reported values. Using cohesive energy calculation, the structural stability of cell is determined. The cohesive energy value for binary CaTe and ternary Ca$_{0.875}$Ba$_{0.125}$Te alloy is 3.73eV/atom and 3.68eV/atom respectively.

| Table 1. Lattice constant $a_0$(Å$^*$), bulk modulus B(GPa) and B’ and band gap $E_g$ (eV) for CaTe and Ca$_{0.875}$Ba$_{0.125}$Te alloys. |  |  |
|---|---|---|
|  |  |  |
Alloy | Present | CaTe | Other study | Ca₀.₈₇₅Ba₀.₁₂₅Te | Present study
--- | --- | --- | --- | --- | ---
\(a₀(A⁰)\) | 6.398 | 6.348[14] | 6.396[1] | 6.396[18] | 6.451
B(GPa) | 35.689 | 41.8[14] | 39.6[1] | 38.7[18] | 34.521
B' | 5.3675 | | | | 4.5764
\(Eₜ\) (eV) | 1.587 | 1.53[1] | 1.578[18] | | 1.647

3.2. Electronic properties

Density of states (DOS) calculations and electronic/band structure calculations are done by FP-LAPW scheme associated with GGA is presented in Fig. 1 and 2. The DOS below Fermi level (0 eV) is called as the valence band owing to the fully filled states on the other hand, DOS above the Fermi level (0 eV) is called as the conduction band because of the unoccupied states. In CaTe alloy which is shown in Fig. 1a, below the Fermi level is mostly due to the Te- 5s & 5p states and above the Fermi level is mainly due to the Ca- 4s & 3d states whereas in ternary Ca₀.₈₇₅Ba₀.₁₂₅Te alloy (Fig. 1b), lower the Fermi level is primarily due to Te- 5s & 5p states and little bit contribution from Ba- p & d states and above the Fermi level is owing to Ca- d & Ba- d states. From Fig.1a, it can be observed that the strong hybridization occurs between Ca-d and Te-d states indicate covalent bonding nature of the atoms. Similarly, from Fig.1b, one can noticed that the charge transfer from Ca atom to Ba atom at Fermi level indicates the covalent nature of the atoms.

![Figure 1a. Total density of states of CaTe.](image)

![Figure 1b. Total density of states of Ca₀.₈₇₅Ba₀.₁₂₅Te.](image)

The self-consistent relativistic energy band gap (\(E₉\)) of the CaTe and Ca₀.₈₇₅Ba₀.₁₂₅Te alloys were calculated and presented in Table 1, and verified with the theoretically calculated values and experimentally determined data. The electron effective mass plays vital role in lowest sharp band in conduction band, whereas mixture of sharp and flat band plays major role in maximum of valence band along the same symmetry. The combination of flat and sharp band enhances the electron transport, as the flat band is responsible for the higher value of electron electrical conductivity. Thus, the hybrid band is more effective for solar cell materials. The maximum of valence band and the minimum of conduction band for Ca₀.₈₇₅Ba₀.₁₂₅Te alloy is situated at Γ point, ensuing in a direct band gap, whereby
in case of parent compound CaTe, the nature of the band gap is indirect such that the VBM lying at \( \Gamma \) point and CBM is at the X point of the Brillouin zone.

To understand the chemical bonding nature between atoms, charge density plots are drawn for parent CaTe and ternary Ca\(_{0.875}\)Ba\(_{0.125}\)Te alloys as shown in Fig. 3a and b respectively. From Fig. 3a, it is observed that the directional charge density contour that encloses the Ca and Te atoms indicates the hybridization between Ca- d and Te- d states. It reveals the covalent nature of the material. In Fig. 3b, it is clearly seen that the covalent interaction occurs between Ca with Ba atoms, due to charge transfer from Ca atom to Ba atom.

3.3. Optical properties

The following optical properties namely complex dielectric function, optical conductivity, absorption coefficient and energy loss function are calculated for CaTe and Ca\(_{0.875}\)Ba\(_{0.125}\)Te alloys. The optical properties calculations performed with no intra band contributions added. Complex dielectric function \[\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega)\] is determined by the transition from the valence to conduction band. Real part of the dielectric function corresponds to dispersive behaviour and the
imaginary part corresponds to the absorptive behaviour of the material. Static dielectric constant is the most important quantity in real part of the dielectric function, which strongly depends on the energy gap and it is given (from Fig. 4) 6.5 and 6.6 for CaTe and Ca$_{0.875}$Ba$_{0.125}$Te alloys respectively. The absorption coefficient determines the ability of material to absorb the incident photon of specific frequency [23]. It can be seen in Fig. 5a, the absorption part of binary CaTe and ternary Ca$_{0.875}$Ba$_{0.125}$Te spectra starts with nearly 1.8 eV(CaTe) and 1.75 eV (Ca$_{0.875}$Ba$_{0.125}$Te) respectively. The combined graph of optical conductivity (sigma) and energy loss function (E$_{{\text{loss}}}$) of the CaTe and Ca$_{0.875}$Ba$_{0.125}$Te alloys are shown in Fig. 5b. In binary CaTe, E$_0$ = 1.587 eV, the first peak appears for 4.5 eV and the optical conductivity has the maximum value of 7450 [1/(Ohm cm)], whereas in Ca$_{0.875}$Ba$_{0.125}$Te, E$_0$ = 1.633 eV, the first peak appears for 4.7 eV and the optical conductivity(sigma) has the maximum value of 6500 [1/(Ohm cm)] corresponds to visible region of the electromagnetic spectrum. Fast electron energy-loss which is moving in the material is explained by the energy loss spectrum [23]. The main peak which is known as bulk plasma frequency occurs at zero point of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ and minimum reflectivity. In Fig. 5b, the main peak of energy loss spectrum of CaTe and Ca$_{0.875}$Ba$_{0.125}$Te is roughly located at 13 eV and 12.5 eV respectively.

3.4. Mechanical and Elastic properties
Elastic constants of solids determine the crystal response for external forces and play vital role in strength and stability of the materials. To study the stability of cubic CaTe and Ca$_{0.875}$Ba$_{0.125}$Te compounds, the cubic three independent elastic constants namely $C_{11}$, $C_{12}$ and $C_{44}$ are calculated. The calculated elastic constants satisfy the stability criteria [24]. Using elastic constants [25], one can determine the mechanical properties such as shear modulus (G), Young’s modulus (E), Cauchy pressure ($C_{12} - C_{44}$), G/B ratio, Poisson’s ratio ($\nu$), Hardness (H$_V$) and anisotropy factor (A) and these computed values for CaTe and Ca$_{0.875}$Ba$_{0.125}$Te alloys are given in Table 2. The higher shear modulus indicates the noticeable directional bonding between atoms [24] and it provides better relation with hardness. Bulk modulus is the ratio of volume stress to volume strain and it measures the resistance to volume by means of applied pressure. Young’s modulus is the ratio of longitudinal stress and longitudinal strain in a material and it has an impact on the ductility. From Table 2, the analysis on modulus values and hardness indicates that the stiffness, strength of covalent bond and hardness of the ternary Ca$_{0.875}$Ba$_{0.125}$Te is decreased. Anisotropy factor $A=1$ indicates an isotropic material, whereas the change of value 1 shows the degree of the material’s anisotropy. It can be seen from Table 2, the CaTe and Ca$_{0.875}$Ba$_{0.125}$Te are known as anisotropy materials owing to Anisotropy factor $A < 1$.

The ductile nature and brittle behaviour of the material is investigated by the three main factors such as Cauchy’s pressure ($C_{12} - C_{44}$), degree of brittleness (G/B ratio) and Poisson’s ratio ($\nu$) and all the three calculated values are shown in Table 2. When $C_{12} - C_{44}$ values are negative, G/B ratio is greater than 0.57 and Poisson’s ratio is less than 0.3, the material exhibits brittle nature. From the above study, one can confirm that the both materials parent binary CaTe and its ternary Ca$_{0.875}$Ba$_{0.125}$Te alloy are brittle in nature, in which ternary Ca$_{0.875}$Ba$_{0.125}$Te alloy is less brittle than the parent binary CaTe.

### Table 2. Calculated elastic and mechanical properties of CaTe and Ca$_{0.875}$Ba$_{0.125}$Te

| Alloy         | CaTe Present work | CaTe Other work | C$_{40.875}B_{0.125}$Te Present work |
|--------------|-------------------|-----------------|-------------------------------------|
| $C_{11}$ (GPa) | 92.28             | 89.26[1]        | 82.26                               |
| $C_{12}$ (GPa) | 10.73             | 14.77[1]        | 11.21                               |
| $C_{44}$ (GPa) | 27.84             | 18.52[1]        | 22.23                               |
| G (GPa)       | 32.45             |                 | 26.85                               |
| E (GPa)       | 75.75             |                 | 64.09                               |
| $C_{12} - C_{44}$ (GPa) | -17.10           | -11.22          |                                     |
| G/B           | 0.86              | 0.77            |                                     |
| N             | 0.17              | 0.19            |                                     |
| H$_V$         | 9.10              | 5.56            |                                     |
| A             | 0.68              | 0.55            |                                     |

3.5. Thermal properties

The following thermal properties namely longitudinal ($V_L$) and shear sound velocities ($V_S$), Debye average velocity ($V_d$), Debye temperature ($\theta_D$) [26], melting temperature ($T_m$) and Gruneisen parameter ($\zeta$) [27] have been calculated for CaTe and Ca$_{0.875}$Ba$_{0.125}$Te alloys and presented in Table 3. Debye temperature is correlated to the strength of covalent bonds and it is used to measure the thermal conductivity of materials. The direct relationship between Debye temperature and average sound velocity indicates that the larger the average sound velocity, the larger the Debye temperature. The
measure of the anharmonicity of the crystal is known as Gruneisen parameter (ζ). The value of Gruneisen parameter (ζ) varies with respect to the elastic moduli through sound velocities. Therefore, the larger Gruneisen parameter (ζ) and smaller Debye temperature (θD) represent the soft bonding nature of the crystal.

Table 3. Calculated V_L, V_S, and V_m, ΘD, T_m and ζ of CaTe and Ca_{0.875}Ba_{0.125}Te

| Alloy                        | CaTe          | Ca_{0.875}Ba_{0.125}Te |
|------------------------------|---------------|------------------------|
| V_L (10^3 m/s)               | 8.741         | 6.928                  |
| V_S (10^3 m/s)               | 5.525         | 3.827                  |
| V_m (10^3 m/s)               | 6.079         | 3.294                  |
| ΘD (K)                      | 568           | 423                    |
| T_m (K)                     | 1398          | 1339                   |
| ζ                           | 1.168         | 1.657                  |

4. Conclusion
Structural, electronic, mechanical, optical and thermal properties of binary CaTe and ternary Ca_{0.875}Ba_{0.125}Te alloys are investigated by using generalized gradient approximation (GGA). The calculated cohesive energy of CaTe and Ca_{0.875}Ba_{0.125}Te compounds shows that the structures have mechanical stability. From the outcomes of DOS and band calculations, it can be concluded that the ternary Ca_{0.875}Ba_{0.125}Te combination is a direct band gap (1.647 eV) semiconducting material with covalent bonding character. Because of the band matching with the incident light energy, the direct band gap has a technological significance and the existence of sharp band in conduction region and the hybrid band in valence region increases the electron transport. To determine the optical properties of CaTe and Ca_{0.875}Ba_{0.125}Te alloys, the optical parameters such as dielectric constants, absorption coefficient, optical conductivity and E_{loss} function are calculated for photon radiation up to 13.0 eV. The other important features of Ca_{0.875}Ba_{0.125}Te are the maximum sigma occur at lower photon energy and the maximum E_{loss} occur at higher energy. Hence, the calculated electronic and optical properties of Ca_{0.875}Ba_{0.125}Te show that it is a suitable material for optical devices and solar cell applications.

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