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A comparative DFT study on electronic, thermodynamic and optical properties of telluride compounds

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ABSTRACT

A detail and comparative study on electronic, thermodynamic and non-linear optical (NLO) properties of seven telluride compounds, viz., XTe (X = Bi, Cd, Pb, Zn), X_2Te_3 (X = Bi, Sb) and $X_2Y_xTe_{3-x}$ (X = Bi, Y = Se, x = 0 to 0.3) are performed under the density functional formalism. Various electronic, thermodynamic and NLO parameters are utilized for the prediction of best telluride candidates towards different application directions. A very popular hybrid exchange–correlation functional B3LYP, as proposed by Becke, is employed for these purposes under the density functional theory (DFT). It is evident from the present study that CdTe is the best candidate for possible conductivity whereas Sb_2Te_3 is found to be the most favorable for NLO materials. Also, it is noticed that Se doping enhances the optical activities in Bi_2Te_3.

1. Introduction

Tellurides are the class of chemical compounds, which comprises metals and the element tellurium [1]. Telluride ions (i.e., Te^{2-}), when combined with their various electropositive counterparts, e.g., Bi^{3+}, Sb^{3+}, Zn^{2+} etc., form different telluride compounds with several important applications [2]. Various telluride compounds have gained lots of attention for their possible applications as semiconductor, thermoelectric materials, spintronics, photovoltaic materials and also as the topological insulators [3–13]. The phase transitions and vibrational properties of MTe (M = Zn, Cd, Hg) are studied under local density approximation [3]. Also, elastic, electronic and optical properties of ZnTe have been investigated by Khenata et al. [4]. It is shown that Bi_2Te_3 is a narrow gap semiconductor and behave like an efficient thermoelectric material when alloyed with selenium or antimony [5]. PbTe p–n junctions are investigated for infrared detections by Barros et al. [6]. Telluride compounds like Bi_2Te_3 and Sb_2Te_3 are well known for their thermoelectric nature at room temperature and finds applications in various devices like thermoelectric generators, thermal sensors, thermopiles, cooling devices etc. [7]. Telluride compounds are also possess eligibility for applications ranging from spintronics to quantum computation [8,9]. CdTe is one of the widely employed photovoltaic materials and thin films of CdTe are being studied for its potential use in solar cells for space applications [10]. In addition, CdTe also finds application in room temperature X-ray and gamma-rays detection, non-destructive testing techniques, industrial imaging etc. [11]. The compounds like Bi_2Te_3, Sb_2Te_3 and Bi_2Se_2Te forms new generation materials, which can show topological insulating effect in the absence of magnetic field [12,13].

Investigations are tendered in search of the potential and possible applications of various telluride compounds through both the experimental and theoretical approaches [14–22]. Larson and Mahanti [14] have studied electronic structure and thermoelectric power of $BaBiTe_3$ and its parent Bi_2Te_3 using density functional theory (DFT). A DFT based study on the electronic structure of small Cd_nTe_n ($1 \leqslant n \leqslant 6$) clusters is performed by Bhattacharya and Kshirsagar [15]. Experimental study on CdTe nanocrystals by Gao and Kirstein [16] suggests that its photoluminescence efficiency strongly depends on the pH value of the colloidal solution. A joint experimental and theoretical study is also performed by Lalitha and co-workers [17] to understand the crystal structure, band parameters, electronic and optical properties of thermally evaporated CdTe thin films. The use of CdTe is also found to be cost effective in solar cells [18]. Leitsmann and Ramos [19] have investigated structural and energetic properties of PbTe/CdTe interfaces consisting two different cubic crystal structures with partially ionic bonds. Schrier and Demchenko [20] have studied optical properties of ZnTe toward photovoltaic applications. They have applied band-corrected pseudopotential DFT calculations to understand how the band gap, optical absorption, and carrier localization can be controlled by forming quantum-well like and nanowire-based heterostructures of ZnO/ZnS and ZnO/ZnTe [18]. Thermoelectric

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properties are studied for Bi_2Te_3 atomic quintuple thin films [21]. A combined spectroscopic ellipsometry and DFT investigation on the optical properties and band structure of Sb_2Te_3 is carried out by Park and co-workers [22].

Although a number of works has been done on deciphering the properties of specific telluride compounds, detailed comparative study for a series of telluride family with the goal of favorable candidate prediction, is not yet performed. Along this direction, we have utilized DFT to perform a detailed investigation on finding the structure, electronic, thermodynamic and optical properties of a series of seven telluride compounds comprising of three different classes, viz., I. (1:1) tellurides: *X*Te (*X* = Bi, Cd, Pb, Zn), II. (2:3) tellurides: X_2Te_3 (*X* = Bi, Sb) and III. doped telluride: $X_2Y_xTe_{3-x}$ (*X* = Bi, *Y* = Se, *x* = 0–0.3) to ensure the most favorable candidates for different aspects of applications.

2. Computational details

Density functional theory (DFT) [23] with a popular gradient corrected approximation is utilized for the calculation of different electronic, thermodynamic and optical properties of the considered tellurides. A molecular orbital approach, using a linear combination of atomic orbitals (LCAO), is applied to probe the electronic structure. For exchange and correlation functional, we have used a very popular and successful hybrid functionals, B3LYP (Becke's three parameter exchange with Lee–Yang–Parr correlation functional) [24]. A very useful and well established effective core potential for the heavier elements, viz., LANL2DZ (Los Alamos National Laboratory 2-double-zeta) [25] is utilized as the basis set for all the considered compounds.

For the electronic descriptors, we have considered HOMO–LUMO energy gap (HLG), ionization potential (*IP*), electron affinity (*EA*), chemical potential (μ), electronegativity (χ), chemical hardness (η) and electrophilicity index (ω), for all the telluride compounds.

The ionization potential (*IP*) and electron affinity (*EA*) can be expressed in terms of the highest occupied (ϵ_{HOMO}) and the lowest unoccupied (ϵ_{LUMO}) molecular orbital energies using Koopmans' approximation [23] as,

$$IP \approx -\epsilon_{HOMO}; \quad EA \approx -\epsilon_{LUMO} \tag{1}$$

The chemical potential (μ) and electronegativity (χ) are defined as [23],

$$\mu = -\chi = \left(\frac{\delta E}{\delta \rho}\right)_{v(\vec{r})} \tag{2}$$

where *E* and $v(\vec{r})$ are the total energy and external potential respectively. Using a finite difference approximation, μ and χ may be expressed in terms of *IP* and *EA* as:

$$\mu = -\chi = -\frac{IP + EA}{2} \tag{3}$$

To account for the stability of a molecule, Pearson [26] has introduced two parameters, viz., 'chemical hardness (η)' and 'chemical softness (*S*)'. For an *N*-electron system, the second derivative of energy with respect to *N*, keeping external potential $v(\vec{r})$ fixed, is considered to be a measure of the chemical hardness (η) [27]:

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} \tag{4}$$

Hardness (η) can also be expressed in terms of (ϵ_{HOMO}) and (ϵ_{LUMO}), implying a finite difference approach [23], as follows:

$$\eta \approx \frac{IP - EA}{2} \approx \frac{\epsilon_{LUMO} - \epsilon_{HOMO}}{2} \tag{5}$$

The inverse of hardness [28] can be defined as softness, $S = \frac{1}{2\eta}$. Parr and Szentpaly defined electrophilicity index (ω) [29] as:

$$\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}, \tag{6}$$

which measures the stabilization in energy when the system acquires an additional electronic charge ΔN from the environment.

For the thermodynamic properties, we have studied temperature dependence (within the range of 200–400 K) of specific heat (C_V), enthalpy (*H*), Entropy (*S*) and Gibbs free energy (*G*), for all the telluride compounds [30,31].

For the optical properties, we have predicted dipole moment (*p*), polarizability (α) and hyperpolarizability (β) for all the compounds [32,33]. A non-linear dielectric medium is characterized by a non-linear relation between polarization density and electric field. Although for a small amount of applied electric field (***F***), dipole moment (*p*) shows a linear behavior to ***F***, the relation becomes non-linear when ***F*** acquires a value comparable to the interatomic electric fields ($\boldsymbol{F_i}$) [32].

The electric dipole polarizability (α) can be calculated as [23,33]:

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{7}$$

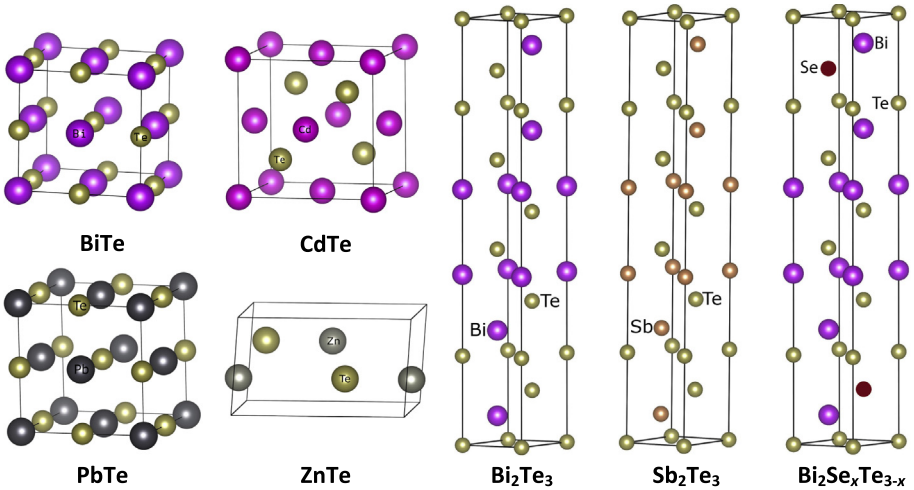

Fig. 1. Unit cells of various telluride compounds.