



Feasibility of crystalline isostructural $X_2Sb_2Te_5$ ($X = Ge, Si$) phase change materials in memory storage devices: First principles calculations



Sonal Talreja^a, Khushboo Sharma^b, B.L. Ahuja^{a,b,*}

^a Computer Centre, Vigyan Bhawan, M.L. Sukhadia University, Udaipur 313001, India

^b Department of Physics, University College of Science, M.L. Sukhadia University, Udaipur 313001, India

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ABSTRACT

We have investigated the electronic and optical response of two isostructural non-volatile memory compounds, $Ge_2Sb_2Te_5$ and $Si_2Sb_2Te_5$, by employing the full potential linearized augmented plane wave method. Self consistent first-principles calculations were performed for the first time by using modified exchange potential of Becke and Johnson namely mBJ potential. Topology of energy bands and density of states of both the compounds are discussed. The optical properties such as dielectric constants, refractive indices, reflection spectra, extinction coefficients are also discussed in order to throw more light on the applicability of these compounds in memory storage devices.

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1. Introduction

Phase change (PC) chalcogenide alloys are known to be important materials for storing information in current multimedia applications, such as optical and electrical memory devices (DVD-RAM, DVD-RW, Blu-Ray Disc) [1–7]. Also, the phase change random access memory (PCRAM) using PC materials as record media is an emerging non-volatile computer memory technology [8]. A deep understanding of electronic and optical properties of PC materials like $Ge_2Sb_2Te_5$ (GST) and $Si_2Sb_2Te_5$ (SST) is quintessential for tuning their properties.

GST is known to exist in two crystalline phases, namely a metastable cubic phase and a stable hexagonal phase. In the past, three atomic arrangements of the GST have been proposed. Earlier, in a study reported by Petrov et al. [9], the authors have proposed an atomic sequence of Te–Sb–Te–Ge–Te–Te–Ge–Te–Sb– for the GST compound. Also, it was reported that the GST has a hexagonal structure with space group $P\bar{3}m1$ and lattice parameters $a = 4.20 \text{ \AA}$ and $c = 16.96 \text{ \AA}$. After several years, Kooi and De Hosson [10] argued on the positions of Ge and Sb atoms in the earlier proposed stacking [9] and further suggested a stacking sequence Te–Ge–Te–Sb–Te–Te–Sb–Te–Ge– by interchanging the positions of the two atoms (Ge and Sb) in the GST. However, Matsunaga

et al. [11] have suggested a stacking sequence of Te–Sb/Ge–Te–Sb/Ge–Te–Te–Sb/Ge–Te–Sb/Ge with Ge and Sb randomly occupying the same layer. Further, the first-principles calculations based on the density functional theory (DFT) to compare the previously proposed models have been reported by Sun et al. [12] and Sosso et al. [13]. In both the studies, the authors have concluded that the most stable configuration of GST is the one proposed by Kooi and De Hosson [10]. Considering this stable configuration of GST [10], Sa et al. [14] proposed the same stacking configuration for SST as no other structural information was reported for this material. Also, Lee et al. [15] have reported the experimental investigation of the optical and electronic properties of GST in different phases. A detailed theoretical investigation on the global and local structures of the Ge–Sb–Te ternary alloy system using self-consistent *ab initio* pseudo-potential method has been reported by Eom et al. [16]. Zhang et al. [17] have carried out Fourier transform infrared spectroscopy of SST and reported band gap in polycrystalline SST as 0.62 eV. A study on the electronic and atomic structure of the crystalline (cubic) and amorphous phases of GST using the CASTEP code has been reported by Robertson et al. [18]. Further, a density functional study of the GST (including crystalline phase) has been reported by Akola and Jones [19] using the Car–Parrinello MD package (CPMD). Lee and Jhi [20] have carried out an *ab initio* study of the structural, electronic and optical properties of the cubic and hexagonal structures of GST using pseudopotential DFT method. Further, the authors have reported the energy gap of 0.26 eV for the most stable layer sequence of GST. Da Silva et al. [21] have used the first-principles calculations to identify the mechanisms that

* Corresponding author at: Department of Physics, University College of Science, M.L. Sukhadia University, Udaipur 313001, India. Tel.: +91 9414317048; fax: +91 294 2411950.

E-mail address: blahuja@yahoo.com (B.L. Ahuja).

lead to the lowest energy structures for the stable and metastable $(\text{GeTe})_m(\text{Sb}_2\text{Te}_3)_n$ compounds. Piccinini et al. [22] have reported the band calculations for GST using local density approximation (LDA) within Quantum Espresso code and also using restricted Hartree–Fock approximation within linear combinations of atomic orbitals scheme. Caravati et al. [23] have reported first principles study of GST using hybrid exchange–correlation functional (HSE03), particularly to study effect of stoichiometric defects in GST. The electronic and optical properties of the hexagonal and rocksalt-like GST chalcogenide have been studied by Tsafack et al. [24] using the first-principles calculations as implemented in the Quantum Espresso code. The authors have reported a semi-metal behavior of the hexagonal GST compound. A study of crystal and electronic structures and optical properties of GST using the hybrid density functional as implemented in VASP code with the calculated band gap of 0.37 eV has been reported by Kaewmaraya et al. [25]. Recently, Sa et al. [26] have investigated the electronic structure of stable trigonal GST using DFT with Grimme’s semi-empirical correction (DFT-D2 method) on the van der Waals interactions. Vora-ud et al. [27] have studied the electronic structure of GST using discrete variational (DV)-X α molecular orbital method and found a negligible band gap of GST (0.016 eV).

The earlier work on electronic and optical properties of GST reported by several authors, using different types of exchange and correlation functionals, predicts the band gap between 0.016 and 0.50 eV [13,20,24–27]. To the best of our knowledge, very little work on electronic and optical properties of SST is available in the literature. Therefore, to shed more light on the comparative study of electronic and optical response of GST and SST ternary semiconductor alloys, we have attempted more-accurate first-principles calculations using FP-LAPW method. In the present computations, we have used the modified version of the original Becke–Johnson (BJ) exchange potential [28] also known as mBJ (modified Becke–Johnson) potential [29] which is considered to be quite precise in elaborating electronic and optical properties of insulators and semiconductors as compared to various schemes within GGA and LDA. The main objectives of the present work were:

- To study the electronic and optical properties of GST and SST using the latest mBJ potential, which is considered to be more accurate in predicting these properties as compared to other potentials used in DFT calculations.
- To compute integrated absorption coefficients and reflectivity of GST and SST materials for feasible colored laser lights and justify their applicability in non-volatile memories.

2. Computational aspects

Fig. 1(a) and (b) depict the crystal structure of $\text{X}_2\text{Sb}_2\text{Te}_5$ (X = Ge, Si) with space group $\text{P}\bar{3}\text{m}1$ (Te–X–Te–Sb–Te–Te–Sb–Te–X– stacking configuration) and the corresponding Brillouin zones. To determine the electronic and optical properties, we have used the FP-LAPW method as incorporated in the Wien2k code [30,31]. In the FP-LAPW method, the unit cell is divided into non-overlapping muffin-tin (MT) atomic spheres and interstitial region. The wave functions are expanded in terms of spherical harmonics within the MT spheres, whereas in the interstitial region these are taken like plane waves. For better accuracy of present calculations than the available data, we have employed the latest exchange–correlation potential, namely the mBJ potential [29]. The mBJ potential is defined as,

$$v_{x,n}^{\text{mBJ}}(r) = c v_{x,n}^{\text{BR}}(r) + (3c - 2) \frac{1}{\pi} \sqrt{\frac{5}{12}} \sqrt{\frac{2t_n(r)}{\rho_n(r)}} \quad (1)$$

where $\rho_n = \sum_{i=1}^{N_n} |\phi_{i,n}|^2$ is the electron density and $t_n = (1/2) \sum_{i=1}^{N_n} \nabla \phi_{i,n}^*$ with $\nabla \phi_{i,n}$ being kinetic-energy density. $v_{x,n}^{\text{BR}}(r)$ is the Becke–Rousell (BR) potential [32].

This new orbital independent exchange–correlation potential, depending entirely on the semilocal quantities, is known to improve the values of band gap of semiconductors [29,33–35] and therefore their optical properties. In the present work, automatically generated k points from $10 \times 10 \times 10$ Monkhorst–Pack sampling in the irreducible BZ was used for the self-consistent field computations. For Fourier expansion of potential in the interstitial region, the plane wave cut off parameters were decided by $R_{\text{MT}} * K_{\text{max}} = 7$ (where R_{MT} is radius of MT sphere and K_{max} represents the magnitude of the largest reciprocal vector in the plane wave expansion) and $G_{\text{max}} = 12 \text{ a.u.}^{-1}$. Also, the wave function inside the sphere was expanded until $l_{\text{max}} = 10$ and the total energy was converged to less than 10^{-4} Ry .

The linear response of a material to the electromagnetic radiations is well characterized by the dielectric function [36], which also governs the propagation behavior of radiations in a medium. The frequency dependent complex dielectric function $\epsilon(\omega)$ is sum of real (ϵ_1) and imaginary (ϵ_2) components. The absorption of light in a crystal can be effectively represented by $\epsilon_2(\omega)$, which is derived from the momentum matrix elements between the occupied and unoccupied states. The $\epsilon_1(\omega)$ determines the behavior of dispersion of the electromagnetic energy on penetration into a medium. Further, $\epsilon_1(\omega)$ can be deduced from $\epsilon_2(\omega)$ using the Kramers–Kronig transformation as given below,

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} M \int_0^\infty \frac{\epsilon_2(\omega') \omega' d\omega'}{\omega'^2 - \omega^2} \quad (2)$$

where M represents the principal value of the integral.

Further, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are used to calculate other frequency dependent optical properties, like refractive index $n(\omega)$, extinction coefficient $k(\omega)$, optical reflectivity $R(\omega)$, and absorption coefficient $\alpha(\omega)$. It may be noted that the $\alpha(\omega)$ estimates the extent of penetration of energetic photon in the specimen before its absorption. The $n(\omega)$ is a measure of the speed of light through the specimen and the $k(\omega)$ corresponds to the amount of absorption loss when the light photon propagates through the specimen.

Since intraband transitions are important in metals only, these are not considered in the present analysis. Also, due to the insignificant contribution of the scattering of photons involved in the indirect interband transitions, only the direct interband transitions are considered to explain the absorptive part $\epsilon_2(\omega)$.

3. Results and discussion

3.1. Energy bands, density of states and band gap

This section highlights the contrast in the electronic properties of both the isovalent compounds which form the basis of the noticeable difference in their optical properties. Both GST and SST have the similar arrangement of the atoms in the unit cell (Fig. 1(a)) with the replacement of X by Ge or Si in $\text{X}_2\text{Sb}_2\text{Te}_5$ compounds. From Fig. 1(a), it can be seen that the unit cell consists of 9 layers with a space group of $\text{P}\bar{3}\text{m}1$. In the present calculations, we have considered $\text{X}_2\text{Sb}_2\text{Te}_5$ compound consisting of Te–X–Te–Sb–Te–Te–Sb–Te–X– arrangement, as it leads to the lowest value of total energy of the system [12,13]. The theoretical lattice parameter “ a ” and the Wyckoff positions used in the present calculations were taken from Sosso et al. [13] and Sa et al. [14] for GST and SST, respectively.

The energy bands along high symmetry directions of BZ for GST and SST are shown in Figs. 2(a) and 3(a), respectively, while partial and total density of states (DOS) are depicted in Figs. 2(b) and 3(b).

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