Hybrid density functional study of electronic and optical properties of phase change memory material: Ge$_2$Sb$_2$Te$_5$

T. Kaewmaraya, 1  M. Ramzan, 1  H. Löfås, 1  and Rajeev Ahuja$^{1,2}$

1Department of Physics and Astronomy, Box 530,
Uppsala University, S-751 21 Uppsala, Sweden
2Department of Materials and Engineering,
Royal Institute of Technology (KTH), S-100 44 Stockholm, Sweden

In this article, we use hybrid density functional (HSE06) to study the crystal and electronic structures and optical properties of well known phase change memory material Ge$_2$Sb$_2$Te$_5$. We calculate the structural parameters, band gaps and dielectric functions of three stable structures of this material. We also analyze the electron charge distribution using the Bader’s theory of charge analysis. We find that hybrid density functional slightly overestimate the value of 'C' parameter. However, overall, our results calculated with the use of hybrid density functional (HSE06) are very close to available experimental values than calculated with the use of PBE functional. Specifically, the electronic band gap values of this material calculated with HSE06 are in good agreement with the available experimental data in the literature. Furthermore, we perform the charge analysis and find that naive ionic model fails to explain the charge distribution between the constituent atoms, showing the complex nature of this compound.
I. INTRODUCTION

Ge$_2$Sb$_2$Te$_5$ (GST) chalcogenides have been of technological importance due to their applications for rewritable data-storage devices such as compact-disk (CD) and digital versatile disk (DVD). The underlying principle behind the data-storage process is based on the fast and reversible phase transformation between a crystalline phase and an amorphous phase, leading to changes in electrical conductivity and optical reflectivity [1–3]. In particular, the phase change happens at relatively low temperature range [4–6], making it feasible for phase change random access memory (PCRAM). More physical understanding of both amorphous and crystalline GST have been essentially needed since it could guide us to further enhancement.

The GST crystalline phase consists of two states namely metastable phase and stable phase. Based on high-resolution electron microscopy analysis, the metastable phase has been proposed to crystallize in the rocksalt-type structure (Fm$\overline{3}$m) that Te atoms completely occupy the 4(a) site and Ge, Sb, and intrinsic vacancies randomly atoms completely occupy the 4(b) site. On the other hand, the stable phase crystallizes in the hexagonal structure. Three different atomic arrangements have been proposed. I. I. Petrov et al. [8] firstly performed an experiment by using electron transmission microscope and they reported that GST is the hexagonal structure with space group P$\overline{3}$m1 having corresponding lattice constants $a = 4.20$ Å and $c = 16.96$ Å, respectively. Te atoms occupy 1(a), 2(d), and 2(d) sites while Sb and Ge atoms occupy 2(d) and 2(c) sites. Later, B. J. J. Kooi et al. [9] argued that Ge atoms occupy 2(d) sites and Sb atoms occupy 2(c) sites. However, T. Matsunaga et al. [10] further investigated this by x-ray diffraction and they found different results. According to them, GST crystallizes in hexagonal structure with the space group P$\overline{3}$m1 and the lattice parameters $a = 4.2247$ Å and $c = 17.2391$ Å. They have also indicated that Ge and Sb atoms randomly occupy 2(d) and 2(c) sites. Up to now, complete explanations of atomic arrangement of the GST stable phase has remained unclear. However, B. S. Lee and co-workers [6] and J. W. Park et al. [11] experimentally studied the electronic and optical properties of the stable GST phase. In addition, there are also theoretical investigations related to the stable GST phase. Z. Sun et al. [12] carried out first-principles electronic structure calculations based on the density functional theory (DFT) to compare three proposed models and they have concluded that the configuration proposed by Kooi et al. [9] is the most stable one.

Hybrid functional of J. H. Heyd, G. E. Scuseria and M. Ernzerhof, better called HSE06 [13] has been shown to give improved structural parameters for a number of systems as compared to the local density approximations (LDA) and Generalized gradient approximation (GGA) [14, 15].
In addition, they also provide improved band gaps which are close to experiment, slightly lower for most cases \cite{14, 15}. Up to now, no theoretical studies have been conducted to investigate the structural and optical properties of GST material by using hybrid density functionals. In this work, we therefore perform the calculations to address structural and electronic properties of stable GST using GGA and hybrid density functional (HSE06). The optimized structural parameters and electronic structures are presented. Finally, the optical properties of this compound are also investigated.

II. METHODS/COMPUTATIONAL DETAILS

*Ab-initio* total energy calculations based on the density functional theory (DFT) \cite{16} and all-electron projector-augmented wave method \cite{17} have been performed by using the VIENNA AB INITIO SIMULATION PACKAGE (VASP) \cite{18, 19}. The atomic structures were constructed according to the experimental data provided by refs. \cite{8–10}. The generalized gradient approximation of Perdew Burke-Ernzerhof (PBE) \cite{20} was employed as exchange-correlation functionals. 14 electrons ($3d^{10}4s^24p^2$) of Ge, 5 electrons ($5s^25p^3$) of Sb, and 6 electron ($5s^25p^4$) of Te were treated as valence electrons in the pseudopotentials. The cutoff energy for plane wave basis of 800 eV and the k-point mesh for brillouin zone integration of 8x8x2 were used since they provide sufficient convergence in total energy of structural optimization. On the other hand, the denser k-point mesh of 16x16x8 was adopted for calculating density of states (DOS) and dielectric functions.

Calculations using hybrid density functional (HSE06) \cite{13} were also comparatively carried out. In this particular case, the exchange-correlation functionals are the rational mixing between the Fock exchange, PBE exchange and PBE correlation

$$E_{xc}^{HSE} = \frac{1}{4} E_x^{HF,SR} (\mu) + \frac{3}{4} E_x^{PBE,SR} (\mu) + E_x^{PBE,LR} (\mu) + E_c^{PBE},$$ (1)

The PBE exchange term is decomposed into two parts namely short range (sr) and long-range (lr) while the correlation part is totally from PBE. The parameter $\mu$ represents the range when the short range term is negligible and it is 0.207$^{-1}$ for HSE06. The detailed mathematical derivations and tests of HSE06 functionals are given in ref. \cite{13}. In order to obtain satisfactory results with reasonable computing time, the lower cutoff energy and k-point mesh, 600 eV and 4x4x2, respectively were used for structural optimization. The denser k-point mesh was adjusted higher to be 8x8x2 for calculating DOS and dielectric functions. The conjugate gradient scheme utilized for electronic relaxation algorithm is applied to all the structural optimization. The volume, shape, and
atomic positions were fully optimized and relaxations were allowed until the Hellmann-Feynman forces on the atoms were less than 0.005 eV/Å. In addition, the calculated electronic charge density from the optimized atomic structure was used to calculate electronic charge partitioned for each atom by using a grid-based Bader charge analysis \[21, 22\]. The zero flux surface of the electronic charge density is used to determine the amount of charge occupied by that particular atom.

### III. RESULTS AND DISCUSSION

We start our calculations by optimizing atomic structures of the stable phase of GST proposed in references \[8–10\] and they are labeled as A (I. I. Petrov et al. \[8\]), B (B. J. Kooi et al. \[9\]), and C (T. Matsunaga et al. \[10\]), respectively. The equilibrium geometries by using PBE and HSE06 functionals are given in \[1\]. It can be seen that the unit cell (1 formula unit) consists of 9 atoms (2 Ge, 2 Sb and 5 Te). The stable GST is a layered structure that Ge, Sb, and Te atoms are stacked along \(c\)-axis (in the \([0001]\) direction). The optimized lattice parameters are listed in \[1\] PBE functionals obviously overestimate lattice parameters with the maximum 2 % difference as compared to the reported experimental values. This comes from the well-known deficiency that GGA functionals overestimate lattice constants. However, we have found that our calculations are in good agreement with those previously reported calculations as also indicated in \[1\]. However, using the HSE06 functional, the lattice constant \(a\) is improved to be closer to the experimental values, but the lattice constant \(c\) is overestimated. This could be related to that the stable GST is a layered structure along \(c\)-axis. The interactions between adjacent layers are probably low and hybrid functional may fail to explain these weak interactions.

After acquiring the complete information about structural parameters, we proceed to investigate the corresponding electronic structures of these stable phases of Ge\(_2\)Sb\(_2\)Te\(_5\). Our calculated density of states (DOS) with the use of PBE and HSE06 functionals of these stable phases are shown in \[2\]. We see that PBE and HSE06 give almost similar DOS and it is found that Te-derived states are mainly formed at the top of the valence band while Ge, Sb, and Te share the bottom of conduction band. However, there is strong hybridization of Sb and Te atoms in the conduction band around 0.5-1.0 eV for A and C whereas Ge, Sb, and Te atoms almost equally hybridize for B. This can be explained by their different atomic arrangements. For A, Sb atoms from 2(d) sites are surrounded by Te atoms from 1(a), 2(d), and 2(d) sites. For B, Sb atoms from 2(c) site are surrounded by Te atoms from 1(a) site. In addition, states in the conduction band have very similar shapes but they are pushed upward, resulting in higher band gaps as indicated in \[1\] PBE functional predicts band
gaps as 0.00 eV, 0.24 eV, and 0.22 eV for A, B, and C, respectively while it has been reported that stable GST has the band gap ranging from 0.50-0.57 eV\[6, 11\]. The band gaps are quantitatively underestimated because of the main deficiency of DFT to deal with excitation. However, HSE06 hybrid functional gives band gaps closer to the experimental values found in the literature. The C phase has the band gap of 0.48 eV which is in good agreement with the experimental values while B phase has slightly lower, 0.37 eV. On the other hand, the phase A has the smallest band gap of 0.26 eV.

In 3, we show the real and imaginary parts of dielectric functions of Ge$_2$Sb$_2$Te$_5$. The left side represents the dielectric functions calculated by using PBE functional whereas the right side denotes those calculated by using hybrid density functional. For PBE functional, A and C have nearly similar dielectric functions. They have the same amplitude of the real part dielectric function at zero energy and their main peaks of the imaginary part are located between 1.5-2.0 eV, in good agreement with reported results in ref. \[11\]. However, the main peak of the imaginary part of B is slightly lower than A and C. It has been experimentally reported that the imaginary dielectric function locates at 1.5 eV\[11\]. For HSE06 functional, It is found that A, B, and C, have slightly different dielectric functions considering in terms of the locations of main peaks of the imaginary part, the starting point at zero energy of the real part and the amplitudes.

We have also calculated the electronic charge distribution by using Bader Charge analysis\[21, 22\] and list our results in III. As mentioned earlier that Ge, Sb, and Te have 14, 5, and 6 valence electrons, respectively. In a pure ionic model, Ge and Sb would loose 4 and 3 electrons respectively and Te may gain $\approx$ 3 electrons. But in our case the situation is rather complex. For instance in phase A, Ge and Sb are loosing only 0.31 and 0.6 electrons respectively, which are gained by Te. These results represent the complex nature of this material and reveal the importance of quantitative analysis over a simple ionic model. In the three proposed stable phases of this material, the charge distribution is almost same. Although, the values obtained for B phase favors slightly the charge transfer from Ge and Sb to Te, but the numbers are not fundamentally different from those, which were calculated for A and C structures.

IV. CONCLUSIONS

In summary, we have performed comparative study of the structural, electronic and optical properties of the stable structures of Ge$_2$Sb$_2$Te$_5$, with the use of GGA and hybrid density (HSE06) functionals. In our present study, we have shown that structural parameters and electronic band
gap of this material calculated with the use of hybrid density functional (HSE06) are in good
agreement with the available experimental results than calculated with the use of PBE functional.
However, HSE06 functional slightly overestimate the C parameter and optical properties of this
compound. We have also analyzed the charge distribution between the constituent elements of this
material using the Bader’s theory of atoms and we find that, due to the complex nature of this
compound, the simple ionic model fails to explain it. We have shown that, on the overall, hybrid
density functional (HSE06) is important for the correct description of GST material and especially
to reproduce the electronic structure of this compound. Finally, we have presented that all the
calculated parameters of stable phase B of Ge$_2$Sb$_2$Te$_5$ are more closer to available experimental
data than stable phases A and C.

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Table I. The calculated structural parameters of the stable Ge$_2$Sb$_2$Te$_5$ phase.

| Proposed structures | xc-functionals | $a_0$ (Å) | $c_0$ (Å) |
|---------------------|----------------|----------|----------|
| A                   | PBE            | 4.263    | 17.971   |
|                     | PBE$^c$        | 4.270    | 17.720   |
|                     | HSE06          | 4.216    | 17.832   |
|                     | Experiment$^a$ | 4.200    | 16.960   |
| B                   | PBE            | 4.300    | 17.237   |
|                     | PBE$^c$        | 4.290    | 17.250   |
|                     | HSE06          | 4.230    | 18.058   |
|                     | Experiment$^b$ | 4.200    | 16.960   |
| C                   | PBE            | 4.278    | 17.743   |
|                     | PBE$^d$        | 4.270    | 17.890   |
|                     | HSE06          | 4.204    | 18.196   |
|                     | Experiment$^c$ | 4.220    | 17.240   |

$^a$Experiment in Ref. [8].
$^b$Experiment in Ref. [9].
$^c$Experiment in Ref. [10].
$^d$DFT calculations in Ref. [11].
$^e$DFT calculations in Ref. [23].

Table II. The calculated band gap energies of the stable Ge$_2$Sb$_2$Te$_5$ phase.

| Proposed structures | PBE (eV) | HSE06 (eV) |
|---------------------|----------|------------|
| A                   | 0.00     | 0.26       |
| B                   | 0.24     | 0.37       |
| C                   | 0.22     | 0.48       |

| Experiments         | 0.57 (Ref. [11]), 0.50 (Refs. [6]) |
Table III. The calculated electronic charges of the stable Ge$_2$Sb$_2$Te$_5$ structures by Bader charge analysis.

| atomic species | A    | B    | C    |
|----------------|------|------|------|
| Ge(1)          | 13.69| 13.60| 13.66|
| Ge(2)          | 13.69| 13.60| 13.66|
| Sb(1)          | 4.40 | 4.35 | 4.40 |
| Sb(2)          | 4.40 | 4.35 | 4.40 |
| Te(1)          | 6.52 | 6.44 | 6.49 |
| Te(2)          | 6.29 | 6.37 | 6.32 |
| Te(3)          | 6.29 | 6.37 | 6.32 |
| Te(4)          | 6.36 | 6.46 | 6.37 |
| Te(5)          | 6.36 | 6.46 | 6.37 |

Figure 1. The optimized atomic structures of Ge$_2$Sb$_2$Te$_5$ proposed by (A) I. I. Petrov et al. [8], (B) B. J. Kooi et al. [9] and (C) T. Matsunaga et al. [10]. Red, blue, and pink spheres represent Ge, Sb and Te atoms, respectively.
Figure 2. Density of states (DOS) of Ge$_2$Sb$_2$Te$_5$ calculated with PBE (left side) and HSE06 (right side). The fermi level is shifted to zero.

Figure 3. The real and imaginary parts of dielectric functions of Ge$_2$Sb$_2$Te$_5$ calculated with PBE (left side) and HSE06 (right side).