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Citation: J. Appl. Phys. 109, 023502 (2011); doi: 10.1063/1.3533422
View online: http://dx.doi.org/10.1063/1.3533422
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v109/i2
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Effective coordination concept applied for phase change \((\text{GeTe})_m(\text{Sb}_2\text{Te}_3)_n\) compounds

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(Received 30 September 2010; accepted 1 December 2010; published online 18 January 2011)

In this work, we employed the effective coordination concept to study the local environments of the Ge, Sb, and Te atoms in the \(\text{Ge}_m\text{Sb}_{2n}\text{Te}_{m+3n}\) compounds. From our calculations and analysis, we found an average effective coordination number (ECN) reduction of 1.59, 1.42, and 1.37, for the Ge, Sb, Te atoms in the phase transition from crystalline, ECN=5.55 (Ge), 5.73 (Sb), 4.37 (Te), to the amorphous phase, ECN=3.96 (Ge), 4.31 (Sb), 3.09 (Te), for the \(\text{Ge}_2\text{Sb}_2\text{Te}_5\) composition. Similar changes are observed for other compositions. Thus, our results indicate that the coordination changes from the crystalline to amorphous phase are not large as previously assumed in the literature, i.e., from sixfold to fourfold for Ge, which can contribute to obtain a better understanding of the crystalline to amorphous phase transition. © 2011 American Institute of Physics.

[doi:10.1063/1.3533422]

I. INTRODUCTION

The ternary \(\text{Ge}_m\text{Sb}_{2n}\text{Te}_{m+3n}\) (GST) compounds, which combine the physical and chemical properties of the chalco- genide GeTe and \(\text{Sb}_2\text{Te}_3\) compounds, Fig. 1, is the basis material for optical storage devices, namely, compact disks, digital versatile disks, and Blu-ray disks.1,2 Those applications are only possible due to the fast and reversible resistance change between a crystalline GST phase with low resistivity and an amorphous GST phase with high resistivity.3

Recently, GST compounds have been considered as one of the most important candidates for the development of non-volatile memory devices,4 which have motivated a great effort to improve the stability and speed of the crystalline to amorphous phase change.

There is a consensus from experimental and theoretical studies that Ge atoms change its atomic coordination environment from octahedron in the crystalline phase to about fourfold environments in the amorphous phase,5–9 however, it is still in bedate the mechanism that drives this large coordination environment change. Based on x-ray diffraction study, extended x-ray absorption fine-structure spectroscopy, and structural coordination analysis, Kolobov et al.5,10 suggested that the crystalline to amorphous phase transition is related to an umbrella-flip of Ge atoms from octahedral to tetrahedral sites without the rupture of strong covalent bonds. The umbrella-flip model was recently supported by theoretical calculations. Based on static and molecular dynamics (MD) first-principles calculations, Da Silva et al.11 confirmed that the phase transition is driven by the atomic displacement of Ge atoms along the rocksalt (RS) \([111]\) direction (hexagonal \([0001]\) direction) from stable octahedron (sixfold) to high-energy unstable tetrahedron (fourfold) sites close to the intrinsic vacancy regions (originated from \(\text{Sb}_2\text{Te}_3\)). These atomic displacements generates a high energy intermediate phase between the crystalline and the amorphous phase. Due to the instability of Ge at the tetrahedron sites, the Ge atoms naturally shift away from those sites, giving rise to the formation of local-ordered fourfold motifs and the long-range structural disorder in the amorphous phase.

We want to point out that those large environmental changes are not a rule for crystalline to amorphous phase transitions. For example, MD first-principles calculations, as those performed for the GST compounds,9,10,12,14 have showed that the octahedron motifs (an anion surrounded by six cations) present in the crystalline phase of \(\text{In}_3\text{ZnO}_5\) \((R=\text{In},\text{Ga},\text{Al},n=\text{integer})\) are preserved in the amorphous phase, i.e., there is no abrupt change in the coordination environments as in the GST compounds.15 Thus, it indicates that it is important to quantify the magnitude of the environmental changes in the GST compounds in order to obtain a better atomistic understanding of the phase transition.

As expected, this untypical behavior of the GST compounds have motivated several analysis of the coordination number (CN), however, large discrepancies between theoretical and experimental, as well as between theoretical results can be observed. For example, for amorphous \(\text{Ge}_2\text{Sb}_2\text{Te}_5\), MD first-principles calculations yield atomic structures with \(\text{CN}_{\text{Ge}}=4.2,3,9,3.75,10,5.25–5.75,11,12,14\) while experimental studies reported \(\text{CN}_{\text{Ge}}=3.9\pm0.8,6,13 \) and \(3.85,11\) Similar discrepancies are present for Sb and Te atoms, which can be attributed to the cutoff distance parameter to calculate the CN, as well as differences in the MD calculations. For example, Akola et al.11 used a cutoff distance parameter of 3.20 Å to calculate the CNs for all species (Ge, Sb, Te) in the amorphous \(\text{Ge}_2\text{Sb}_2\text{Te}_5\), which yields \(\text{CN}_{\text{Ge}}=4.2,3.7,2.9\) for Ge, Sb, and Te, respectively, while for the crystalline phase, they reported \(\text{CN}=6.0,6.0,4.8\) for Ge, Sb, and Te, respectively.

The reported values for CN are very sensitive to the cutoff parameter. For example, in the lowest energy crystal structures for \(\text{Ge}_2\text{Sb}_2\text{Te}_5\),14 the largest \(\text{Ge}–\text{Te}\) and \(\text{Sb}–\text{Te}\)
The Ge, Sb, and Te atoms are indicated employing a conventional hexagonal unit cell representation. 

In order to obtain a better understanding of the CNs at different environments for the GST compounds, we will employ the effective coordination concept, which yields the effective CN (ECN) and it does not depend on the choice of a cutoff distance parameter. Thus, we expect that this simple concept can solve some of the problems mentioned above, and hence, contribute to obtain a better understanding of the phase transition problem. To achieve our goals, we considered three GST compositions, namely, Ge$_2$Sb$_2$Te$_5$, GeSb$_2$Te$_4$, and GeSb$_4$Te$_7$ at the crystalline and amorphous phases, and the parent compounds (GeTe, Sb$_2$Te$_3$) were studied as references. From our calculations and analysis, we found an average coordination reduction of 1.59, 1.42, and 1.37, for the Ge, Sb, Te atoms in the phase transition from crystalline to the amorphous phase for the Ge$_2$Sb$_2$Te$_5$ composition, which is smaller than previous results. Similar changes are observed for other compositions.

II. EFFECTIVE COORDINATION CONCEPT

In the standard coordination concept an unique weight ($w_{ij}=1.0$) is attributed for all bond lengths between the atom $i$ and the surrounding $j$ atoms, $d_{ij}$, with bond lengths smaller than a cutoff parameter, $d_{cut}$. Thus, the CN can be obtained by counting the number of bond lengths smaller than $d_{cut}$ and hence, the CN has only integer values. Therefore, this concept can be applied easily for symmetric structures in which the $d_{cut}$ parameter can be easily defined from the first nearest neighbors (NNs) distances, however, for distorted structural motifs such as in the GeTe, Sb$_2$Te$_3$, and GST compounds, the atom $i$ is surrounding by $j$ atoms at different distances, i.e., long and short bond lengths in GST compounds are assumed to contribute with the same weight for the CN. Thus, the choice of the $d_{cut}$ parameter can play an important role in the value of CN for distorted structures, which might explain the discrepancies in the CN results for the GST compounds.

In contrast, in the effective coordination concept, a different weight is calculated for each bond length $d_{ij}$ by using a weight function, i.e., $w_{ij} \neq 1.0$ for all $ij$. This approach is based on the fact that a particular atom $i$ binds stronger with the closer $j$ atoms, and hence, small changes in the coordination environments can be taken into account. All $w_{ij}$ are calculated with respect to the atom weighted bond length, $d^w_{ij}$, which must be calculated for each atom $i$. For example, bond lengths smaller (larger) than the local weighted bond length, $d^w_{cut}$, contribute with a $w_{ij}$ larger (smaller) than the unit. The ECN for a particular atom $i$ (ECN$_i$) is obtained by the sum of all weights, $w_{ij}$, and hence, it is not necessarily an integer value. Thus, this concept can be applied for symmetric or distorted structures consistently.

Different weight functions can be used to obtain the ECN$_i$ with the condition that the selected function should describe the relative weights contributions of the different bond lengths. In this work, we will use an exponential function and power six to obtain ECN$_i$ for all atoms, which was initially introduced in inorganic Chemistry few decades ago, and carefully tested for the most common Bravais lattices in this work. The ECN$_i$ is obtained by the following set of equations,
$\text{ECN}_i = \sum_j \exp \left[ 1 - \left( \frac{d_{ij}}{d_{av}} \right)^6 \right], \quad (1)$

where $d_{ij}$ is the distance between atom $i$ and $j$, while $d_{av}$ is defined as

$$d_{av} = \frac{\sum d_{ij} \exp \left[ 1 - \left( \frac{d_{ij}}{d_{av}} \right)^6 \right]}{\sum \exp \left[ 1 - \left( \frac{d_{ij}}{d_{av}} \right)^6 \right]}. \quad (2)$$

Thus, $d_{av}$ should be obtained self-consistently. In this work, we employed the following stop condition: $|d_{av}^{\text{new}} - d_{av}^{\text{old}}| < 0.0001$. The smallest bond length between the atom $i$ and all $j$ atoms $(d_{\text{min}}^{i})$ is used as the initial value for $d_{av}$ in Eq. (2). The final value of $d_{av}$ is obtained within three to ten iterations for distorted structures with a wide range of different bond lengths, which is then used to obtain ECN$_i$ in Eq. (1).

The average ECN for a particular set of atoms can be obtained by

$$\text{ECN} = \frac{1}{N} \sum_{i=1}^{N} \text{ECN}_i, \quad (3)$$

where $N$ is the number of atoms. We would like to mention that this approach has been employed in the study of transparent conducting oxides and transition-metal clusters with great successful.

### III. Atomic Structures: Computational Details

In this work, we employed structural models for the crystalline and amorphous GST phases obtained by static and MD first-principles calculations based on density functional theory within the generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof. The Kohn–Sham equations were solved using the projected augmented wave method as implemented in the Vienna ab-initio simulation package.

For GeTe and Sb$_2$Te$_3$, we will employ the well known experimental model structures reported by Da Silva et al., while for the amorphous phase, we employed the standard MD first-principles procedure reported in several studies.

In order to obtain a consistent set of atomic structures (equilibrium volumes and atomic positions) of all studied compounds and phases, we re-optimized all model structures using cut-off energies of 576 eV for the stress tensor calculations. For the Brillouin zone integration, we employed high $k$-point densities than employed in Ref. 35, i.e., a $k$-point grid of $(12 \times 12 \times 4)$ for GeTe in the conventional hexagonal unit cell with lattice parameters of $a_0=4.228$ Å and $c_0=10.913$ Å. Similar quality $k$-points, i.e., the same density, were employed for all crystalline and amorphous GST calculations. Compared with previous studies, only the amorphous structures are slightly affected (changes smaller than 1% in the bond lengths) by the reoptimization procedure using high computational parameters. The atomic structures are shown in Fig. 1 for GeTe and Sb$_2$Te$_3$, Figs. 2 and 3 for crystalline stable and metastable GST phases. For the particular case of the amorphous phase, our analysis was applied over three amorphous structures for each GST composition, and the final results are given as average. In Fig. 4 is shown only one structure for each GST composition.

### IV. Results

#### A. ECN applied for simple lattices

To illustrate the use of the effective coordination concept, first, we calculated the CN ($d_{av}=$ first NN distance) and ECN for four well known lattices, namely, simple cubic (sc), face-centered cubic (fcc), body-centered cubic (bcc), and hexagonal close-packed (hcp). The results for CN and ECN are identical for sc, fcc, and hcp lattices, however, it is not the case for bcc, see Table I. For example, we found ECN = 11.63, while CN=8.0 for bcc, which can be attributed to the contribution from the second NN shell to the ECN. From our analysis, ECN of 11.63 can be decomposed as 9.40 from the first NN shell (eight atoms) and 2.23 from the second NN shell (six atoms), i.e., a contribution of about 80% and 20% from the first and second NN shells, respectively. For the other lattices, the contribution of the second NN shell is negligible due to the large second NN distance. For example, in the sc lattice, the first and second NN shells are at $a_0$ and...
The Ge, Sb, and Te atoms are indicated.

\[ a_0 \sqrt{2}, \] while in the bcc lattice, the first and second NN shells are \( a_0 \sqrt{3}/2 \) and \( a_0 \), i.e., the second NN distances are 41.42% (sc) and 15.47% (bcc) larger than the first NN distances.

### B. Crystalline GeTe and Sb\(_2\)Te\(_3\)

GeTe crystallizes in the distorted RS structure with space group \( R3m \),\(^{32,33} \) which has 1 f.u. (where f.u. is formula unit) per primitive rhombohedral unit cell, or 3 f.u. using a hexagonal lattice representation. Table II. For an undistorted RS lattice, the Ge atoms are surrounded by six Te atoms at equal distances, however, the distortion along of the RS \([111]\) direction induces the formation of three short and three long Ge–Te bond lengths (2.855, 3.258 Å). Using \( a_{\text{sc}}=3.30 \) Å, we can obtain \( \text{CN}_{\text{Ge}}=6.0 \), while by taken into account the bond length distortions in the effective coordination concept, we obtained \( \text{ECN}=5.10 \). From our analysis, the three short and three long bonds contribute with 3.68 and 1.41, respectively, i.e., a contribution of about 72% and 28% for the ECN, respectively. Thus, it indicates that the bond is substantially weaker along of the long bond length, which can provides an initial path for a phase transition.

Sb\(_2\)Te\(_3\) crystallizes in a rhombohedral layered structure with space group \( \bar{R} \bar{3} m \) with 1 f.u. (five atoms) per unit cell,\(^{34} \) in which the building blocks (Te–Sb–Te–Sb–Te) have an RS-type structure and are stacked along of the [001] direction in the conventional hexagonal lattice, Table II. The building blocks (Te atoms) are separated by 3.085 Å, which is large compared with Sb–Te interlayer distances (1.706 and 1.990 Å), and hence, it has been suggested that Sb\(_2\)Te\(_3\) is composed by Sb, Te, and intrinsic vacancies ordered in the planes perpendicular to the \( c \) axis, which has been suggested as a consequence of the valence of the Sb (V) and Te (VI) atoms and the electron octet counting rule.\(^{35} \) Using the effective coordination concept, we identified three coordination environments, which is expected. All the Sb atoms have an ECN of 5.89, which is slightly smaller than the coordination of the ideal RS structure (ECN=6.00), i.e., it indicates only a small

<table>
<thead>
<tr>
<th>Stable structures</th>
<th>Metastable structures</th>
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<tbody>
<tr>
<td>( a_0 ) (Å)</td>
<td>( c_0 ) (Å)</td>
</tr>
<tr>
<td>( a_0 ) (Å)</td>
<td>( c_0 ) (Å)</td>
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<td>4.320</td>
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<tr>
<td>Sb(_2)Te(_3)</td>
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</tbody>
</table>
distortion in the octahedrons compared with GeTe. There are
two distinct coordination environments for the Te atoms,
namely, the Te atoms in the center of the building block have
ECN = 6.00 (33% of the Te atoms), while the Te atoms in the
border of the building blocks have ECN = 3.17 (67% of the
Te atoms). We would expect a CN of 3.0 for the Te atoms in
the border of the building block, however, the Te–Te dis-
tances yields a very small contribution, and hence, a value of
3.17 is obtained, which is consistent with the weak van der
Waals binding between the building blocks. Thus, the aver-
age ECN for Te atoms in the Sb2Te3 is 4.11, which is due to
the large number of 3.17-fold Te atoms.

C. GST compounds

For both crystalline (stable and metastable) and amor-
phous phases, there are several Ge, Sb, and Te atoms in the
unit cells, and a wide range of local environments. For the
crystalline phases, the average of the ECN results were per-
formed for sites with similar ECN with the aim to identify
the different local environments, while for the amorphous
phase, the average was performed over all atomic sites with
the same chemical specie due to the wide range of ECN
values. The ECN results are summarized in Table III.

We found similar results for both stable and metastable
crystalline phases, which can be summarized as follows. For
Ge2Sb2Te5, we identified two local environments for the Ge,
Sb, and Te atoms, which would be expected for the Te atoms
due to the presence of intrinsic vacancies but not for the Ge
and Sb atoms. For Ge, ECN increases from 5.10 in GeTe to
about 5.25 (50% of the Ge atoms) and 5.85 (50% of the
Ge atoms), which indicates that the octahedrons are less dis-
torted in Ge2Sb2Te5 than in GeTe. For Sb, we observed an
opposite trend, i.e., ECN decreases from 5.89 in Sb2Te3 to
5.45 (50% of the Sb sites), while the remaining 50% of the
Sb atoms increase its coordination from 5.89 to about 6.00.
As expected for Te atoms, we found lower ECN for the Te
atoms near the intrinsic vacancies, i.e., 3.00 (30% of Te at-
oms), and a higher ECN (5.78), which correspond to the Te
atoms within the building block. Thus, the average ECN for
the Ge, Sb, and Te are 5.55, 5.73, and 4.37, respectively,
which are lower than previous analysis (6.0, 6.0, 4.8) (Refs. 9
and 17) and points out to the importance of the octahedron
distortions and a free parameter approach.

In contrast with Ge2Sb2Te5, we found only a local envi-
ronment for Ge and Sb atoms in the crystalline GeSb2Te4
and GeSb4Te7 compounds, while there are two local environ-
ments for the Te atoms as in Ge2Sb2Te5 due to the presence
of the intrinsic vacancies. For the Ge atoms, we found a
change from ECN = 5.10 in GeTe to 6.00 in GeSb2Te4 and
GeSb4Te7, while the Sb atoms have the same ECN as in
Sb2Te3, i.e., 5.87, as the Sb atoms bind to the threefold Te
atoms. The increase in the Ge coordination is due to the
location of the Ge atoms, i.e., in the center of the building
blocks, which do not provide room for distortion of the oc-
tahedrons. Thus, these results again confirm the import-
ance of the octahedron distortions in the coordination environ-
ments. For Te atoms, we found similar coordination environ-
ment as in the Sb2Te3, i.e., 5.98, 3.00–3.17, however, the
average ECN increases compared with Ge2Sb2Te5.

For the amorphous phases, we found quite similar results
for the studied GST compositions, i.e., ECN = 3.96–4.15 for
Ge, 3.97–4.40 for Sb, and 2.97–3.37 for Te. For all compo-
sitions, we observed a reduction in the average ECN of the
amorphous phase compared with the crystalline phase for all
atomic species, which is consistent with experimental6,18
and theoretical studies.9,17 We would like to point out that the
coordination changes between the crystalline and amorphous
are not large as have been suggested in previous studies. For
the particular case of Ge2Sb2Te5, the ECN reduces from 5.55
(Ge), 5.73 (Sb), and 4.37 (Te) in the crystalline phase to 3.96
(Ge), 4.31 (Sb), and 3.09 (Te) in the amorphous phase. We
can observe an almost constant change in the ECN, i.e., 1.59,
1.42, and 1.37, for Ge, Sb, and Te, respectively. Therefore,
the phase transition from crystalline to the amorphous phase
induces an average ECN reduction in about 1.46 for all
atomic species. Our results for Ge2Sb2Te5 are in excellent
with the results reported by Akola et al.,9 i.e., 4.2 (Ge), 3.7
(Sb), 2.9 (Te), however, in complete disagreement with Sun
et al.17 5.25–5.72 (Ge), 5.67–6.25 (Sb), 3.98–4.46 (Te). It is
unclear the reason of such large discrepancies, however, we
believe that technical computational details might explain
these differences.

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TABLE III. ECNs for the GeTe, Sb2Te3, and GST compounds in the crystalline (stable and metastable) and amorphous phases. For the atomic species (Ge, Sb, Te) with two distinct atomic environments in the crystalline phases, two ECN values are reported in the first and second lines for each composition. The numbers in parentheses indicate the percentage of sites with the respective ECN.

<table>
<thead>
<tr>
<th></th>
<th>Stable phase</th>
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<th>Metastable phase</th>
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<th>Amorphous phase</th>
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<tr>
<td></td>
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<td>Te</td>
<td>Ge</td>
<td>Sb</td>
<td>Te</td>
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<td>GeTe</td>
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<td></td>
<td>5.10</td>
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<td>5.78</td>
<td>(60)</td>
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<tr>
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<td>(50)</td>
<td>6.00</td>
<td>(50)</td>
<td>5.78</td>
<td>(60)</td>
</tr>
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<td>5.29</td>
<td>(50)</td>
<td>5.45</td>
<td>(50)</td>
<td>3.00</td>
<td>(30)</td>
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<td>(50)</td>
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<tr>
<td></td>
<td></td>
<td>3.09</td>
<td>(50)</td>
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<td>3.13</td>
<td>(57)</td>
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<tr>
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<td>5.89</td>
<td></td>
<td>6.00</td>
<td>(33)</td>
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</tbody>
</table>
V. SUMMARY

In summary, we employed the effective coordination concept to calculate the ECN for the Ge, Sb, and Te atoms in the GST compounds in different phases. Our results for ECN do not depend on the cutoff distance parameter currently employed in previous studies. Furthermore, it can take into account short and long bond lengths with different weights, and hence, provides a better description for distorted lattices. We found ECN values for Ge, Sb, and the Te atoms in the crystalline phase smaller than previous results due to the distortions in the octahedrons, which could not be taken in previous studies. For the amorphous phase, our results are slightly larger than previous results, which indicates that the cutoff distance parameter might be a bit small.

Thus, our analysis indicates that the coordination changes from the crystalline to the amorphous phase transition are smaller than previous suggested. Thus, it plays an important role to obtain a better understanding of the phase transition mechanism. For example, in the umbrella-flip model for the Ge atoms, it was suggested that the Ge atoms change from octahedral sites in crystalline GST to tetrahedral sites in amorphous GST without the rupture of strong covalent bonds. Our analysis suggest that this mechanism, which was confirmed by first-principles calculations, might be favored by the presence of long bonds in the GST compounds, which provide a small contribution for the coordination environment.

ACKNOWLEDGMENTS

J. L. F. Da Silva thanks the São Paulo Science Foundation (FAPESP) for the support.


