Initial Structure Memory of Pressure-Induced Changes in the Phase-Change Memory Alloy $Ge_2Sb_2Te_5$

M. Krbal,[1,2] A. V. Kolobov,[2] J. Haines,[1] P. Fons,[2] C. Levelut,[3] R. Le Parc,[3] M. Hanfland,[4]
J. Tominaga,[2] A. Pradel,[1] and M. Ribes[1]

[1]Institut Charles Gerhardt, UMR 5253 CNRS-UM2-ENSCM-UM1, PMDP/PMOF, Université Montpellier II,
Place Eugène Bataillon, Montpellier Cedex 5, France
[2]Center for Applied Near-Field Optics Research (CanFor), National Institute of Advanced Industrial Science and Technology,
1-1-1, Higashi, Tsukuba 305-8562, Japan
[3]Laboratoire des Colloides, Verres et Nanomatériaux, Université Montpellier II,
Place Eugène Bataillon, Montlpellier Cedex 5, France
[4]European Synchrotron Radiation Facility (ESRF), 6 rue Jules Horowitz, Boîte Postale 220, F38043, Grenoble, France

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We demonstrate that while the metastable face-centered cubic (fcc) phase of $Ge_2Sb_2Te_5$ becomes amorphous under hydrostatic compression at about 15 GPa, the stable trigonal phase remains crystalline. Upon higher compression, a body-centered cubic phase is obtained in both cases around 30 GPa. Upon decompression, the amorphous phase is retained for the starting fcc phase while the initial structure is recovered for the starting trigonal phase. We argue that the presence of vacancies and associated subsequent large atomic displacements lead to nanoscale phase separation and loss of initial structure memory in the fcc staring phase of $Ge_2Sb_2Te_5$.

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Ultrafast phase transitions have recently attracted growing attention for designing fast and dense nonvolatile memory devices. Contradictory requirements such as high switching speed and long-term stability have singled out Te-based multicomponent alloys along the GeTe-Sb_2Te_3 quasibinary tieline with the material of choice for *both* electronic and optical memories being $Ge_2Sb_2Te_5$ (GST) [1]. The excellent scalability of phase-change materials has made them a leading candidate for future nonvolatile memories. The importance of phase-change materials for both present and future memory applications clearly requires better knowledge of their fundamental properties and the physics behind the utilized phase transition.

While the stable structure of $Ge_2Sb_2Te_5$ is hexagonal, the metastable cubic phase utilized in devices possesses a distorted rocksalt structure with Te atoms forming one face-centered cubic (fcc) lattice and Ge/Sb/vacancies forming the other fcc lattice [2]. In what follows we refer to this structure as cubic.

Recently, it was shown that cubic $Ge_2Sb_2Te_5$ can also be rendered amorphous under hydrostatic pressure above 10 GPa [3]. It was further demonstrated that the phenomenon is rather general, and can be also observed for other compositions along the quasibinary GeTe-Sb_2Te_3 tieline [4]. Subsequent studies have shown that pressure-induced amorphization does not depend on temperature [5].

In this Letter we compare the behavior of the two phases of $Ge_2Sb_2Te_5$ (metastable cubic and stable hexagonal) under pressure and report on the existence of an the initial structure memory effect with respect to pressure-induced processes in the prototypical phase-change memory material: while compression-decompression cycle for fcc $Ge_2Sb_2Te_5$ is irreversible and upon decompression an amorphous phase predominates, the stable trigonal $Ge_2Sb_2Te_5$ recovers its original crystalline structure under identical conditions.

Measurements were performed at room temperature at beam line ID09A at ESRF (Grenoble, France). The sample consisted of $Ge_2Sb_2Te_5$ and NaCl that was used as a pressure marker. Both materials were placed next to each other in the gasket hole between the anvils of a diamond anvil cell. Helium gas was used as a pressure transmitting medium to ensure the best possible hydrostatic conditions. Debye-Scherrer diffraction images were collected selectively from the $Ge_2Sb_2Te_5$ sample and the NaCl marker with a monochromatic beam ($\lambda = 0.4115$ Å) focused to ca. $20 \times 20\ \mu m$ using a MAR345 online image plate reader. The pressure was increased or decreased in steps of ca. 1 to 2 GPa and the system was allowed to equilibrate for 5 to 10 minutes at each pressure point. The acquisition time was typically 2–10 seconds. The pressure was measured based on the equation of state (EOS) for the B1 [6] and B2 [7] phases of NaCl.

The structural calculations in this work were carried out at 0 K by the *ab initio* total energy, plane-wave, pseudopotential method using the CASTEP code [8]. Ultrasoft pseudopotentials, a plane-wave cutoff energy of 230 eV, and the LDA functional for the electron exchange-correlation energy were used. We used a cell containing 56 atoms ($GeSb_2Te_4$ stoichiometry) and assumed no symmetry in the relaxation process. A $2 \times 2 \times 2$ Monkhorst-Pack grid was used to sample k space.

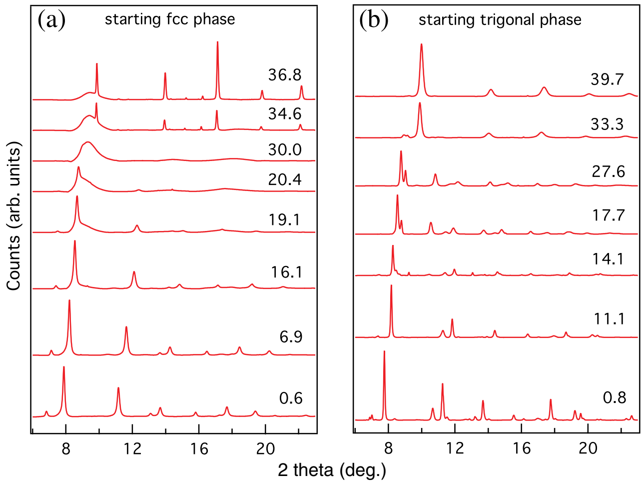

FIG. 1 (color online). Evolution of the x-ray diffraction patterns of the metastable fcc phase (left) and the stable trigonal phase (right) of $Ge_2Sb_2Te_5$ upon compression. The corresponding pressures are marked next to each curve.

The behavior of $Ge_2Sb_2Te_5$ upon compression is shown in Fig. 1. The cubic fcc phase starts to disappear and the amorphous phase grows from about 15 GPa. The amorphization process continues until the crystalline fcc phase totally disappears at 25 GPa [Fig. 1(a)].

Upon further compression of the amorphous phase, a new crystalline phase starts to grow above 33 GPa; however, some amorpohous material remains up to the highest pressures reached. The new crystalline phase is identified as body-centered cubic (bcc) with the space group $Im\bar{3}m, a = 3.38$ Å (at 35 GPa). The diffraction data are consistent with complete disorder on the 2(a) Wyckoff sites. In what follows we refer to this phase as bcc(C), with the C standing for the initial cubic phase.

The trigonal phase, on the other hand, remains crystalline in the pressure range studied. Upon compression at room temperature, the trigonal phase is transformed into an intermediate crystalline phase (orthorhombic GeS type [9]) and subsequently into bcc [Fig. 1(b)]. We refer to this phase as bcc(T).

It is interesting to note that the two high-pressure phases—although both are bcc—possess different diffraction patterns (Fig. 2). While the bcc(C) possesses large crystallites, the starting trigonal phase exhibits fine-powder patterns in all three phases. This difference may be due to the fact that the amorphous phase is uniform and continuous while the orthorhombic phase consists of small grains. It seems natural that larger crystallites can grow within a continuous uniform amorphous network than from a small individual grains when it may be possible that individual grains undergo the phase transition thus preserving the fine-grain structure.

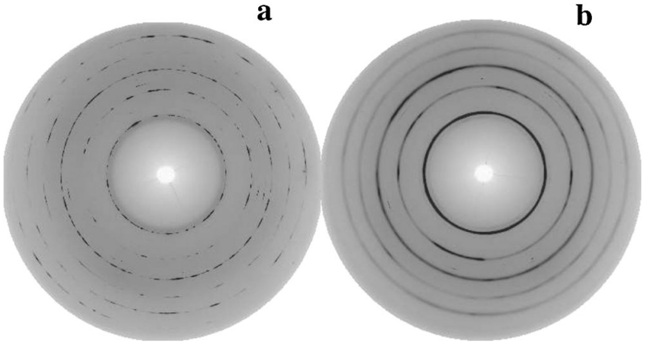

FIG. 2. X-ray diffraction patterns of bcc phases of $Ge_2Sb_2Te_5$ obtained starting with the fcc (left) and trigonal (right) phases.

The decompression behavior is also very different for the two starting structures (Fig. 3). The bcc(T) phase changes into an intermediate crystalline phase and eventually the initial trigonal structure is restored; i.e., pressure-induced changes in the trigonal $Ge_2Sb_2Te_5$ are reversible.

On the other hand, the bcc(C) phase gradually reverts into the amorphous phase with some remaining bcc(C) phase after complete decompression. The crystalline peaks in the completely decompressed bcc(C) phase are located very close to the positions for the NaCl that was used as a pressure marker. To exclude the possibility that $Ge_2Sb_2Te_5$ and NaCl became intermixed during the compression-decompression process, we have remeasured the compression-decompression cycle of metastable cubic $Ge_2Sb_2Te_5$ using Pt as a pressure marker and confirmed that the crystalline peaks are from the $Ge_2Sb_2Te_5$ and not from NaCl.

Different decompression behavior suggests memory of the initial structure: the apparently similar (bcc) structures evolves differently depending on the structure of the initial phase used to generate the high-pressure bcc phase.

The unit cell volume change with pressure is shown in Fig. 4. The fcc $Ge_2Sb_2Te_5$ volume decrease upon initial compression (0 to 13 GPa) can be described by the Birch-Murnaghan equation of state (EOS) [10] with the bulk

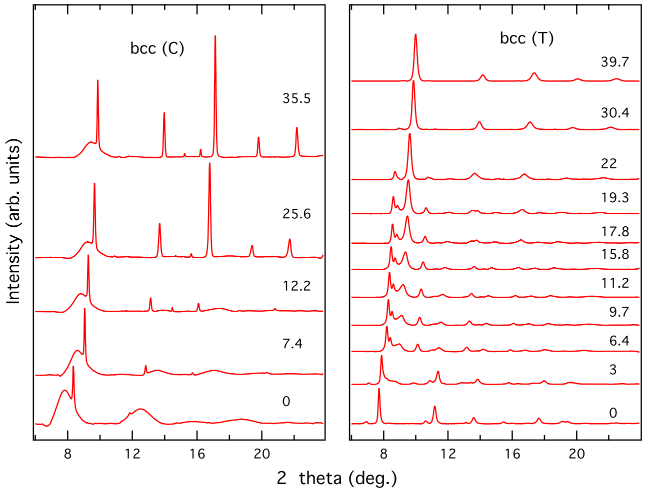

FIG. 3 (color online). Evolution of the x-ray diffraction patterns of the metastable fcc phase (left) and the stable trigonal phase (right) of $Ge_2Sb_2Te_5$ upon decompression. The corresponding pressures are marked next to each curve.

moduli $K_0 = 39 \pm 2$ GPa (Since K_0 and K_0' are strongly correlated and the number of experimental points is rather limited, we have chosen to limit the Birch Murnaghan equation up to 2nd order in elastic strain corresponding to $K_0' = 4$.) These values compare rather well with the known bulk moduli for GeTe ($K_0 = 49.9$ GPa) [11], $AgSbTe_2$ (45 GPa) [12], Sb (39.7 GPa) [13] and our previous laboratory measurement for $Ge_2Sb_2Te_5$ (41 GPa) [3]. At higher pressures (13 to 22 GPa), the volume deviates from the EOS value at lower pressures with the material becoming softer due to partial conversion to the amorphous phase.

In the 33–38 GPa range the much less compressible bcc(C) phase appears. Fitting the data (over a rather limited range) to the EOS yields the following bulk moduli for the high-ressure phase: $K_0 = 61 \pm 10$ GPa (K_0' fixed at 4) and $V/V_0 = 0.88$.

The bulk moduli and normalized volumes obtained for the starting trigonal $Ge_2Sb_2Te_5$ material are as follows (K_0' fixed at 4 in all cases). For the trigonal phase: $K_0 = 44 \pm 2$ GPa ($V/V_0 = 0.95$), for the orthorhombic phase: $K_0 = 48 \pm 6$ GPa ($V/V_0 = 0.91$), and, finally, for the bcc(T) phase: $K_0 = 57 \pm 10$ GPa ($V/V_0 = 0.87$).

The fact that the amorphous phase formed by compression of the fcc phase of $Ge_2Sb_2Te_5$ is actually an intermediate phase between the two crystalline phase deserves special discussion. It strongly suggests that pressure-induced amorphization cannot be treated as "melting" [14]. More likely—as suggested earlier [3]—it proceeds through nanophase separation. Further experimental support of this hypothesis comes from the fact that at 30 GPa the volume of the bcc(C) phase is 1.5% larger than that of the bcc(T) phase. In the case of the bcc(C) the volume tends towards those of bcc Sb (40.6 Å^3) [13] and bcc Te (41.6 Å^3) [15] at 30 GPa. This is an indication that the bcc phase is richer in Sb and Te and that the remaining amorphous material is Ge rich.

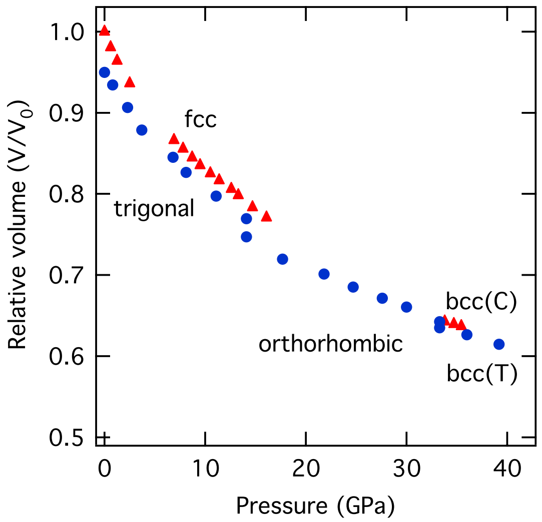

FIG. 4 (color online). Pressure dependence of the normalized volume per (Te) atom (assuming $Ge_2Sb_2Te_5$ stoichiometry throughout the complete cycle) upon compression and decompression for the metastable fcc and stable trigonal phases of $Ge_2Sb_2Te_5$. The error bars are smaller than the size of the symbols used. The triangles correspond to the starting fcc phase and the circles correspond to the starting trigonal phase.

To obtain further insight, we have simulated the pressure-induced change in the fcc phase at 0 K using density functional theory. We have chosen the $GeSb_2Te_4$ composition for the simulations since it allows one to significantly reduce the unit cell volume in the calculations. In the pressure range up to 26 GPa, the system remains in the rocksalt structure although disorder in the atom positions is slightly increased with pressure. Between 26 and 28 GPa strong distortions in the crystal structure are observed and eventually the cubic symmetry is lost. Upon further increase in pressure, the structures changes to bcc (Fig. 5) in agreement with the experimental observations.

Our simulations clearly demonstrate the appearance of a large concentration of Sb-Sb and especially Te-Te bonds; i.e, phase separation of $Ge_2Sb_2Te_5$ indeed takes place upon strong compression. The distribution of bond types is

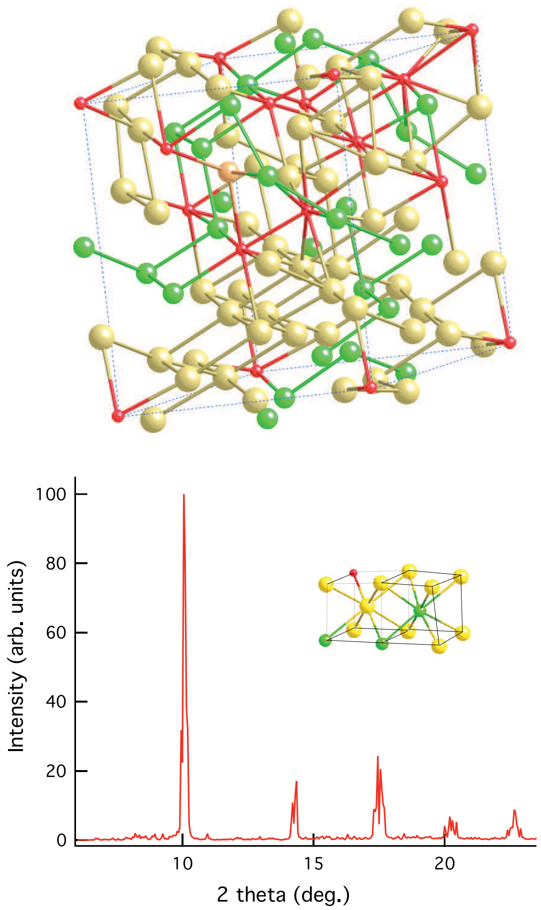

FIG. 5 (color online). The bcc structure (top) and the corresponding diffraction pattern (bottom) for $GeSb_2Te_4$ "compressed" to 46 GPa using DFT simulations (Ge—red, Sb—green, Te—yellow). The insert shows a fragment of the obtained structure with clear bcc arrangement of atoms.

TABLE I. Percentage of different bonds in $GeSb_2Te_4$ at 46 GPa. In cases when the same bonds are listed twice, e.g., Ge-Te vs Te-Ge bonds, one of the numbers is given in parentheses.

Bond type	Ge-Te	Sb-Te	Ge-Sb	Ge-Ge	Sb-Sb	Te-Te
Percentage	22	37	8	1	7	25

shown in Table I. The observed distribution is in good agreement with the conclusion drawn from the experimental data refinement, namely, that the bcc sites are randomly occupied by the three types of constituent atoms. In our high-pressure structure we found no vacant sites; i.e., indeed the pressure-induced change involves vacancy collapse.

The average coordination number in the structure was found to be $CN_{3.0} = 7.2$ for the bond length cutoff of 3.0 Å and $CN_{3.1} = 8.3$ for the cutoff of 3.1 Å. The obtained values are in good agreement with the crystal lattice parameter found from refinement of the experimental data. The first-nearest neighbor distances in the generated structure vary in a range from 2.6 to 3.1 Å demonstrating a very high degree of disorder remaining in the high-pressure phase.

We would like to further stress the important role played by vacancies. Upon compression, the vacancies in the cubic phase can collapse allowing for "giant" atomic rearrangement. It may be informative to mention that pressure-induced amorphization has been observed in a host of materials containing vacancies (voids), e.g., in zeolites [16], porous silicon [17], fullerenes [18], or molecular crystals [19]. The latter do not necessarily contain voids but the molecular fragments are held together by weaker van der Waals interactions with larger interatomic distances; i.e., there are regions with lower density. As a result of large atomic displacements, the new crystalline phase obtained by further compressions "forgets" about the initial crystal structure since the local order of the intermediate amorphous phase is quite different from that of the initial fcc phase [3]. An alternative mechanism should also be considered. Since vacancies in $Ge_2Sb_2Te_5$ serve to electronically stabilize the structure, it may also be possible that their collapse upon compression leads to instabilities in the cubic phase of $Ge_2Sb_2Te_5$ resulting in the destruction of long-range order.

In the trigonal phase, on the other hand, there are no vacancies. For this reason, the structure remains crystalline undergoing a change into an intermediate crystalline phase followed by bcc phase as is also observed for some other materials [15,20]. Upon decompression, the material retransforms back to the initial structure.

To conclude, we have observed a series of pressure-induced phase transitions in the metastable cubic and stable trigonal starting phases of $Ge_2Sb_2Te_5$. At high enough pressures (> 33 GPa) both phases are eventually transformed into bcc. Upon decompression, the bcc(C) phases becomes amorphous while the bcc(T) phase reverts to the starting trigonal phase; i.e., the high-pressure bcc phase possesses memory of the initial structure. We argue that the observed memory (or loss of it) of the initial structure is determined by the presence (or absence) of vacancies and the resulting possibility for "gigantic" atomic motion upon the collapse of the vacancies accompanied by nanophase separation. In a structure with a large concentration of vacancies, atoms "forget" about the initial arrangement while in denser structures without vacancies the atomic motion is limited and atoms retain memory of the initial structure. We believe that the observed effect is of a general nature and can also be detected in other similar systems.

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