

Pressure-induced structural transitions in phase-change materials based on Ge-free Sb-Te alloysMilos Krbal,^{1,2,*} A. V. Kolobov,¹ P. Fons,¹ J. Haines,³ A. Pradel,² M. Ribes,² A. A. Piarristeguy,² C. Levelut,⁴ R. Le Parc,⁴ V. Agafonov,⁵ M. Hanfland,⁶ and J. Tominaga¹¹*Nanodevice Innovation Research Center, National Institute of Advanced Industrial Science and Technology 1-1-1 Higashi, Tsukuba 305-8562, Ibaraki, Japan*²*Institut Charles Gerhardt, UMR 5253 CNRS-UM2-ENSCM-UM1, PMDP, Université Montpellier II, Place Eugène Bataillon, Montpellier Cedex 5, France*³*Institut Charles Gerhardt, UMR 5253 CNRS-UM2-ENSCM-UM1, PMOF, Université Montpellier II, Place Eugène Bataillon, Montpellier Cedex 5, France*⁴*Laboratoire des Colloïdes, Verres et Nanomatériaux, Université Montpellier II, Place Eugène Bataillon, Montpellier Cedex 5, France*⁵*Laboratoire d'Électrodynamique des Matériaux Avancés, UMR CNRS-CEA 6157, F-37200 Tours, France*⁶*European Synchrotron Radiation Facility (ESRF), 6 rue Jules Horowitz, Boîte Postale 220, F-38043 Grenoble, France*

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We report on pressure-induced phase transitions in the Sb_2Te and $\text{Ag}_{11}\text{In}_6\text{Sb}_{55}\text{Te}_{28}$ (AIST) phase change alloys used in optical recording media over a pressure range from ambient pressure to 40 GPa. The results clearly demonstrate the crucial role of dopants in sequences of high-pressure structural transformations and in the degree of reversion. We also demonstrate that prolonged exposure of AIST to high pressures leads to an additional phase transition that may have fatal consequences for process reversibility in repeated compression/decompression cycles.

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I. INTRODUCTION

The Te-based multi-element alloys lying along the $\text{GeTe} - \text{Sb}_2\text{Te}_3$ quasibinary tie-line and Sb-rich Sb-Te (Sb_2Te and AIST)^{1,2} have been intensively studied for their unusual ability to undergo ultrafast phase transitions between amorphous and crystalline phases which are accompanied by drastic changes in optical and electrical properties induced by either optical or electrical pulses. The fast transformation speed, high stability, and excellent scalability of phase-change memory compounds have led to their commercial application in the form of optical storage media such as digital versatile disc random access memory (DVD-RAM), rewritable memory storage (DVD-RW), and Blu-Ray discs³ and to the large-scale investigation of their use in nonvolatile electronic memory devices, often called phase-change random access memory (PC-RAM), which is currently a very hot field of study. 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.

In optical discs, the recorded bits are amorphous marks confined by a crystalline background and cladding layers. The different densities of amorphous and crystalline phases can lead to a significant transient stress in recorded bits on the order of a few GPa.⁴ Also encapsulation materials such as TiN may exert additional compressive stress with values of 240 MPa being reported for a recording film.⁵

The investigation of phase transitions under pressure is of both fundamental and practical interest. Applied pressure can affect reversibly or irreversibly the structure of the crystalline surroundings of the amorphous bit and as well as the stability of the recorded information, as stress may reduce the band gap and makes recrystallization more likely.⁶

Previously, we demonstrated that pressure-induced phase changes in $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ⁷ provided clear evidence that the initial structure of a compound has pivotal importance in the phase transitions that occur upon compression/decompression. We have shown that vacancies present in the rock-salt-like $\text{Ge}_2\text{Sb}_2\text{Te}_5$ structure play a dominant role in the pressure-induced amorphization process⁸ which was shown to be thermally insensitive over the temperature range from room temperature to 145°C.⁹ In this paper, we report pressure-induced phase transitions in Ge-free phase-change materials, namely, Sb_2Te and $\text{Ag}_{11}\text{In}_6\text{Sb}_{55}\text{Te}_{28}$ (AIST), which are widely used in optical memory devices. We demonstrate that albeit the Sb_2Te pressure-induced structural transitions are similar to those observed in trigonal $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ⁷, Ag and In doping of Sb_2Te strongly affects the sequence of structural phases upon compression/decompression. We also demonstrate that prolonged exposure of AIST to compression leads to an additional phase transition that may have negative consequences on the reversibility of the compression/decompression cycle.

II. EXPERIMENTAL DETAILS

The samples for the current experiment were prepared as follows. The Sb_2Te bulk sample was prepared by slow cooling of the molten state of a stoichiometric 2:1 mixture of Sb and Te placed into a quartz ampoule evacuated to 10^{-4} Pa. Both Sb_2Te and AIST films were deposited using rf magnetron sputtering from industrially made targets on SiO_2 substrates. The thickness of the deposited films was about 2 μm . The crystallization process was carried out in a furnace at 470 K for 2 h in a nitrogen atmosphere.

Measurements were performed at room temperature at beamline ID09A at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) using x-rays with a wavelength of $\lambda = 0.4115$ Å over a pressure range from ambient

pressure to 40 GPa. A small amount of the material (Sb_2Te or AIST) and NaCl which was used as a pressure marker 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 at room temperature for the high-pressure measurements. The pressure was increased or decreased in steps of ca. 1 to 2 GPa and allowed to stabilize for 5 to 10 min at each pressure point, which is a typical time range used in similar experiments. The acquisition time was typically 2–10 s; data were taken using an MAR345 image plate system. The pressure was determined based upon the equation of state (EOS) of the B1¹⁰ and B2¹¹ phases of NaCl. In order to obtain additional data, measurements were also carried out using a laboratory-based x-ray source (Mo target with $\lambda = 0.71073 \text{ \AA}$). A 4 : 1 methanol:ethanol mixture was employed as a pressure-transmitting medium and the acquisition time for obtaining one spectrum was 2 days per pressure point. The Rietveld (Le Bail) method was used to obtain accurate lattice parameters on studied samples using the FullProf package.¹²

In this work, pressure-induced phase transitions in the crystalline Sb_2Te bulk sample have been investigated whereas a crystallized film was used in the case of AIST. In order to be sure that results obtained using bulk and film samples were comparable, verification of the initial structures of crystalline Sb_2Te bulk and film materials was carried out which confirmed that the initial states of both compounds had similar structures. For this reason only one of the samples was used in the pressure experiment.

III. RESULTS AND DISCUSSION

A. Sb_2Te

Upon compression, Sb_2Te exhibits three phase transitions [Figs. 1(a) and 1(b)]. The initial crystalline structure of Sb_2Te is a trigonal phase and belongs to the space group $P\bar{3}m1$ with hexagonal lattice constants: $a = 4.274(1) \text{ \AA}$ and $c = 17.652(6) \text{ \AA}$.¹³ The first transition occurs within the pressure range of 7–9 GPa [Fig. 1(a): 9.1 GPa] in which the starting phase becomes orthorhombic and that can be described as the space group $Pbnm$ (GeS-like) with the following lattice parameters: $a = 4.379(9) \text{ \AA}$, $b = 11.309(6) \text{ \AA}$, and $c = 4.173(0) \text{ \AA}$. A similar trigonal \Rightarrow orthorhombic transition was also observed in trigonal $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ⁷ at 17 GPa. The next phase transformation occurred in the pressure range 12.3–15 GPa [Fig. 1(a): 14.4 GPa], where a mixture of orthorhombic and body-centered-tetragonal (BCT) (Sb-II-like) phases can be detected. The BCT phase is an incommensurate composite phase comprising host (space group $I4/mcm$) and guest (space group $I4/mmm$) structures.¹⁴ The refined lattice parameters of the BCT structure at 18.4 GPa were $a_h = a_g = 7.951(4) \text{ \AA}$, $c_h = 3.801(3) \text{ \AA}$, and $c_g = 3.082(7) \text{ \AA}$, yielding a c_h/c_g ratio of 1.233 which is somewhat smaller than the values obtained in other materials with similar structures (1.404 for Sr-V at 56 GPa,¹⁵ 1.309 for Bi-III at 6.8 GPa,¹⁶ and 1.307 for Sb-II at 12 GPa¹⁴). Eventually, the body-centered-cubic (BCC) phase occurs at pressures above 28 GPa [Fig. 1(a): 32 GPa]. This is distinctly different from cubic Ge-Sb-Te alloys that exhibit the formation of an amorphous phase on their route to the high-pressure BCC phase.

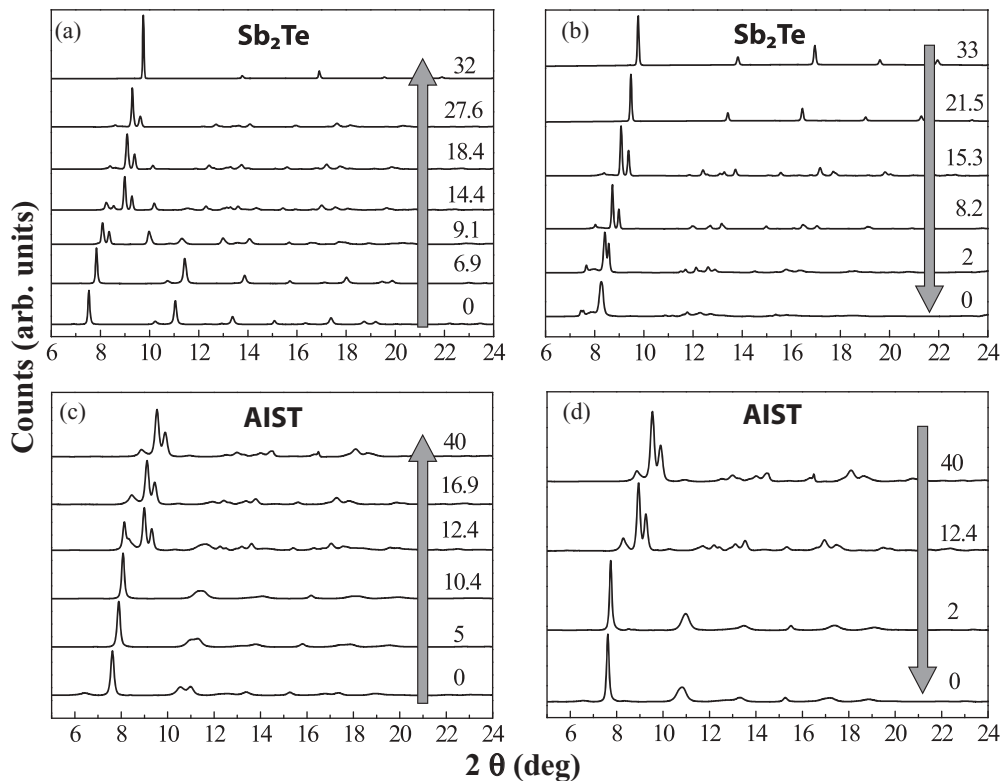


FIG. 1. The evolution of the synchrotron-based x-ray diffraction patterns of Sb_2Te (upper two plots) and AIST (lower two plots) upon compression and decompression. Arrows indicate compression (figures on the left) and decompression (figures on the right).

Upon decompression [Fig. 1(b)], the BCC phase gradually retransforms to the BCT structure over the range of pressures from 21.5 to 15.3 GPa and remains stable to ambient pressure.

B. Ag-In-Sb-Te

The incorporation of elements such as Ag and In into Sb_2Te leads to a change of the initial phase to an A7 structure (rhombohedral) that belongs to the space group $R\bar{3}m$ with the lattice constants $a = 4.307(8)$ Å and $c = 11.214(6)$ Å. Over the studied pressure range of 0–40 GPa only one phase transition was observed at 12.4 GPa with the material adopting the BCT form [Fig. 1(c): 12.4 GPa] with lattice parameters $a_h = a_g = 8.037(1)$ Å, $c_h = 3.866(4)$ Å, and $c_g = 2.984(1)$ Å, giving a c_h/c_g ratio of 1.296. Upon decompression [see Fig. 1(d)], the AIST sample reverted to the initial A7 structure with slightly different lattice constants: $a = 4.348(8)$ Å and $c = 10.975(7)$ Å.

The final fits to the diffraction patterns of all phases observed in Sb_2Te and the AIST alloys upon compression are shown in Fig. 2. The $Pbnm$ space group was used to fit the Sb_2Te orthorhombic structure, although it is apparent that some inaccuracies are present in the calculated profile. Refinements based on other possible symmetries, i.e., the $Pbcn$ ¹⁷ and $Cmcm$ ¹⁸ space groups proposed for GeTe and AgSbTe₂, respectively, yield worse fits with missing peaks.

While Sb_2Te showed similar phase transitions using both synchrotron- and laboratory-based measurements, a new low-pressure phase of AIST was discovered using a laboratory-based x-ray source at 3 GPa which has been identified as simple cubic with $a = 3.023(2)$ Å that transforms to the BCT form upon increasing pressure to 13 GPa. In contrast to the synchrotron-based measurement, the BCT structure remains upon complete decompression. We believe that these differences in the behavior of AIST under pressure can be attributed to the duration of pressure being applied. Upon compression, atomic diffusion is suppressed resulting predominantly in the compression of the unit cell when the pressure is applied for a short time (on the order of minutes to hours), whereas longer times (on the order of days to weeks) of exposure to high pressure likely enable the unit cell to relax to a more suitable crystallographic symmetry. It should be

mentioned that allowing compression to occur for a long time eliminates any remaining atomic configurations of the starting low-pressure form.

The reversion of the A7 \Rightarrow simple cubic \Rightarrow A7 transitions has been studied. The initial A7 structure was compressed to 3.4 GPa and slowly decompressed to ambient pressure. The simple cubic phase was dominant at 3.4 GPa (more than 95% of the mixture) and this state remained even at ambient pressure while part of the simple cubic phase reverted to the A7 structure (the amount of the A7 was estimated to be about 10%).

Although the initial structures of Sb_2Te and AIST are described with different space group symmetries, from the crystallographic viewpoint both the trigonal and rhombohedral phases can be used to represent the same structure. It has been shown that the Sb-rich Sb-Te system perfectly satisfies the $R\bar{3}m$ configuration with the stacking sequences that vary¹⁹ depending on the Sb content. For example, a high-pressure investigation of Sb_2Te_3 ,²⁰ which crystallizes in the A7 structure, transformed at 10 GPa to a crystal modification similar to that found in this work for Sb_2Te at the same pressure and was proposed to be orthorhombic ($Pbnm$). In contrast, the addition of Ag and In into the Sb_2Te system results in a A7 \Rightarrow BCT transition which is probably coupled with a change of the local atomic arrangement around Te, whereas the local structure around Sb is unchanged.²¹ Such local atomic changes can happen in AIST via phase segregation when the amorphous phase is crystallized and the crystalline product could occur as a mixture of an excess of pure Sb and possible compounds such as Ag-Te, AgSbTe₂, AgInTe₂, InSb, and Sb_xTe_y .^{22,23} Such phase separation of Ag-doped chalcogenides accompanied with the formation of Ag-rich phases embedded in a chalcogenide matrix even at very low Ag concentrations has been reported earlier.^{24–26} From the crystallographic point of view, pure Sb possess a rhombohedral symmetry whereas Ag-Te and AgSbTe₂ crystallize into the rock-salt-like structure of which the cation sublattice is disordered. Upon compression, for example, the rock-salt structure of AgSbTe₂ collapses at 17 GPa¹⁸ to form an amorphous phase which is identical to the route that has been observed in rock-salt-like $\text{Ge}_2\text{Sb}_2\text{Te}_5$.^{7,27} Indium-based phases such as AgInTe₂ and InSb are also known with the former being chalcopyrite and the

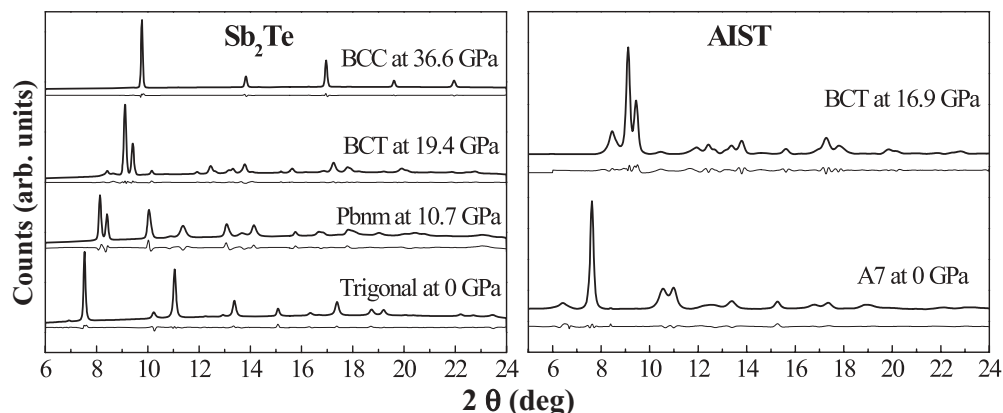


FIG. 2. The final fits to the diffraction patterns of all phases present in Sb_2Te and AIST alloys upon compression observed using synchrotron radiation. The lines under the XRD data show the difference between calculated and measured data for each spectrum.

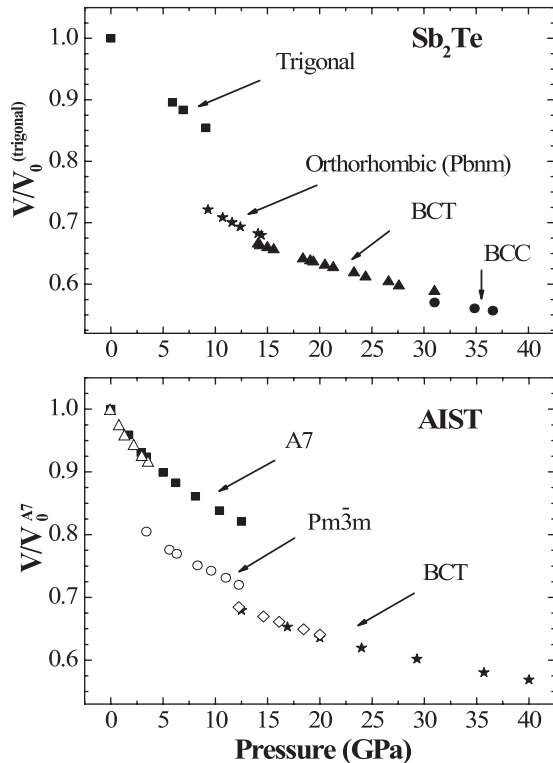


FIG. 3. The pressure dependencies of the relative volume of Sb_2Te and AIST with denoted crystallographic symmetries observed using synchrotron radiation. In the case of AIST, open symbols represent the results obtained using a laboratory x-ray-based source.

latter zinc-blend. Interestingly, both compounds undergo phase transitions at about 2 GPa to the rock-salt-like symmetry²⁸ and β Sn, respectively, while InSb subsequently transforms to a rock-salt-like structure at 8 GPa.²⁹ When pressure is released, reversion of such compressed material to the original state lasts for at least three months.²⁸ These low-pressure transitions along with the long structural recovery are noticeably similar to those observed in the AIST sample under laboratory-based conditions. Thus phase separation, which can appear during the crystallization process or as a consequence of a long duration of applied pressure, could be a possible explanation of the different behaviors of Sb_2Te and AIST at high pressure and might have an impact on reversion when the pressure is released.

The pressure dependencies of the relative volume of Sb_2Te and AIST are shown in Fig. 3. The observed decrease in compressibility can be described by the Birch-Murnaghan EOS.³⁰ (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 to second order in elastic strain corresponding to $K'_0 = 4$.) The obtained values of EOS fitting are presented in Table I.

TABLE I. Bulk moduli and the V/V_0 of respective phases observed in Sb_2Te and AIST upon compression.

Sb_2Te			AIST		
Phase	V/V_0	K [GPa]	Phase	V/V_0	K [GPa]
Trigonal	1	42.8 ± 0.33	A7	1	44.3 ± 1.5
Orthorhombic	0.842	43.7 ± 2	Simple cubic ^a	0.85	53.9 ± 2
BCT	0.782	61.2 ± 1	BCT	0.78	67.7 ± 2.3
BCC	0.744	70.7 ± 5.2	–	–	–

^aThe simple cubic phase occurred when the A7 structure was exposed to pressures above 3 GPa for a few days.

The values for initial structures compare rather well with known bulk moduli in GeTe ($K_0 = 49.9$ GPa),¹⁷ AgSbTe_2 (45 GPa), and¹⁸ Sb (39.7 GPa)¹⁴ and with our previous measurement for $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (41 GPa).⁷ The values of the bulk moduli of the BCT phases are similar in both systems and are a bit lower than that observed in Sb-II (71.2 GPa).

The abrupt decrease of the volume in both systems can be accounted for based on a transformation from layered structures (the trigonal and the A7 phases) to more compact phases [the orthorhombic and the BCT phases (simple cubic)].

IV. CONCLUSIONS

Pressure-induced phase changes in Sb_2Te and AIST have been studied. In contrast to cubic Ge-Sb-Te alloys, Ge-free phase-change materials do not exhibit pressure-induced amorphization. The different behavior upon compression for these materials indicates that a small addition of Ag and In into Sb_2Te changes the initial structure and strongly influences the sequence of high-pressure structures. While Sb_2Te displayed several transitions over the studied range of pressures, AIST transformed from the initial A7 structure to the BCT modification and remained in this symmetry up to 40 GPa. It was found that AIST easily reverted while Sb_2Te retained its high pressure modification when pressure was released. We showed that longer dwell times (on the order of days to weeks) of the A7 phase of AIST at pressures above 3 GPa led to an irreversible A7 to simple cubic transition. The BCT structure of AIST did not revert after being exposed to high pressures for a week.

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