

Pressure-induced changes in phase-change materials

A.V. Kolobov¹, M. Krbal², P. Fons¹, J. Haines², J. Tominaga¹, C. Steimer³, M. Hanfland⁴, G. Aquilanti⁴,
S. Pascarelli⁴, Y. Katayama⁵, A. Pradel², M. Ribes², C. Levelut⁶, R. LeParc⁶

¹ Center for Applied Near-Field Optics Research (CanFor), National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba 305-8562, Japan

² Institut Charles Gerhardt, UMR 5253 CNRS-UM2-ENSCM-UM1, PMDP/PMOF, Universite Montpellier II, Place Eugene Bataillon, 34095 Montpellier Cedex 5, France

³ I. Physikalisches Institut der RWTH Aachen, Lehrstuhl für Physik neuer Materialien, 52056 Aachen, Germany

⁴ European Synchrotron Radiation Facility (ESRF), Grenoble, France

⁵ Synchrotron Radiation Research Center, Japan Atomic Energy Agency, Kouto, 1-1-1, Sayo, Hyogo 679-5148, Japan

⁶ Laboratoire des Colloïdes, Verres et Nanomatériaux, Université Montpellier II, Place Eugene Bataillon, Montpellier Cedex 5, France

ABSTRACT

We report on pressure-induced transformations in Ge-Sb-Te phase-change alloys. Both GST-225 and GST-124 in the metastable cubic structure amorphize under hydrostatic pressure. The process is irreversible, i.e. the decompressed sample stays amorphous. The trigonal structure, on the other hand, remains crystalline under identical conditions. These results suggest a crucial role of vacancies in the pressure-induced amorphisation process. Implications for memory devices are discussed.

Key words: Ge-Sb-Te, pressure-induced amorphisation, vacancies

1. INTRODUCTION

Photoinduced phase transitions are attracting ongoing attention because of their application in storage devices. The properties needed for commercial memory applications, such as fast switching, long-term stability of the photoconverted state, and high level cyclability have singled out phase-change telluride alloys. The most used materials for commercial discs include Ge-Sb-Te (GST) for DVD-RAM and Ag-In-Sb-Te (AIST) alloys for DVD-RW. Interestingly, the same materials give rise to the best performance of the so-called super-resolution near-field structure (Super-RENS) discs that allow the reading of bits beyond the diffraction limit, although the readout mechanism is believed to be different from conventional phase-change memory. Furthermore, the same materials are used in Ovonic Unified memory (OUM). It has even been argued that phase-change memory is likely to replace the presently wide-spread flash memory due to its scalability and potentially unlimited rewrite capabilities.

Since pressure is an important thermodynamical parameter it can be surmised to have a strong effect on phase stability. However, up to now, only the role of temperature has been considered in the phase diagram. We would like to emphasize that pressures momentarily generated in recorded molten bits can reach 5-6 GPa [1].

The stable GST structure is trigonal. At the same time, XRD experiments on thin layers have indicated that they crystallize into a higher-symmetry metastable structure that is similar to the rocksalt structure with Te atoms forming one face-centered cubic (fcc) sublattice and Ge and Sb species occupying sites on the other fcc sublattice with 20 % of the sites in the latter vacant. In this work, we deal mainly with the metastable crystal (cubic) structure that is relevant to phase-change memories. While the local structure of metastable GST is distorted with Ge and Sb atoms displaced from the center of the cell [2-4], long-range order is best described as having the rocksalt structure with a large thermal factor and in what follows we use pseudo-cubic peak indexing.

2. EXPERIMENTS

X-ray diffraction measurements were performed at beamline ID09A at ESRF (Grenoble, France) using a wavelength of 0.4115 Å. The GST sample and NaCl 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 while fluorinert was used for high-temperature high-pressure measurements. Measurements were performed in a pressure range from 0 to 30 GPa at the following temperatures: 25, 68, 111, 145, and 220 °C. The choice of temperatures was determined taking into account the known phase transitions in GST at ambient pressure, namely, crystallization of the amorphous phase into the metastable fcc phase and subsequent transition into the stable trigonal phase. The pressure was increased/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 of 2 - 10 seconds; data were taken using a MAR345 image plate system. The pressure was measured based on the equation of state (EOS) of NaCl [1].

XAFS measurements were performed at Ge K-edge at energy dispersive beamline ID24 at ESRF. The existing equipment also allowed us to measure (although in a rather limited angle range) XRD spectra on the same sample so that we could correlate long-range and short-range structural changes. Additionally, XAFS spectra at all three edges (Ge K-edge, Sb K-edge, and Te K-edge) were also measured in transmission mode at BL14B1 at SPring-8 (0 to 11 GPa pressure range) using a large multi-anvil press.

3. RESULTS & DISCUSSION

Figure 1 shows the pressure-induced evolution of the observed XRD pattern for GST225 and GST124 [5]. One can see that in the pressure range 0 to 10 GPa, compression results in a simple shift of all peaks to larger angles indicating a decrease in the unit cell volume under compression. The bulk moduli K_0 and K' obtained by fitting the Birch-Murnaghan equation of state to the experimental data (Fig. 2) are $K_0 = 41$ GPa and $K' = 3.8$ for both compositions. It may be informative to compare this value with the corresponding values for the bulk trigonal phase of GST(225). As one can see from Fig. 2, all three materials possess rather similar bulk moduli.

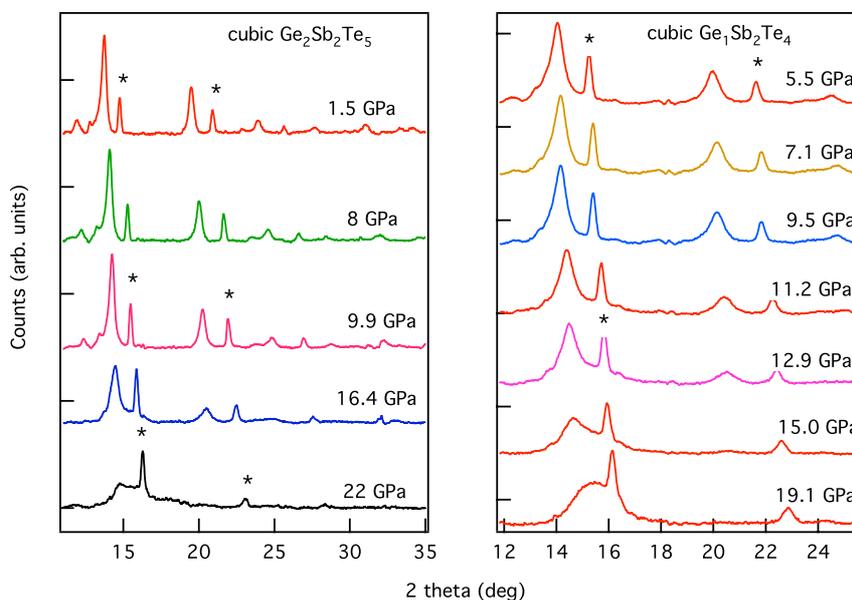


FIGURE 1: Pressure-induced changes of the XRD pattern of GST225 (left) and GST124 (right) upon compression. The peaks marked by * (on some of the spectra) are the corresponding peaks of the NaCl marker. The pressures are shown at the right side of each plot [6].

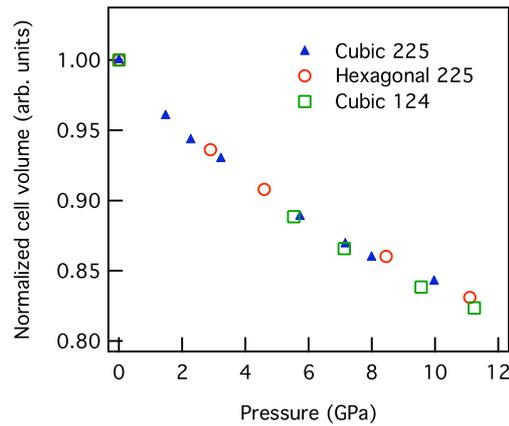


FIGURE 2: Pressure dependencies of the unit-cell volume for metastable cubic phases of GST225 and GST124 as well as for the stable hexagonal phase of GST225.

At higher pressures, the intensity of the GST peaks in the metastable cubic phases decreases, the peaks broaden and eventually are replaced by broad amorphous bands. It should be noted that pressures at which GST amorphises is lower in GST124.

In the temperature range from room temperature to ca. 150 °C, the behavior of GST(225) upon compression is essentially identical. The cubic fcc phase starts to disappear and the amorphous phase grows from 15 GPa. The amorphisation process continues until the crystalline fcc phase totally disappears at ~25 GPa. The onset of the amorphisation and its completion do not depend on temperature in this temperature range (Fig. 3) [6].

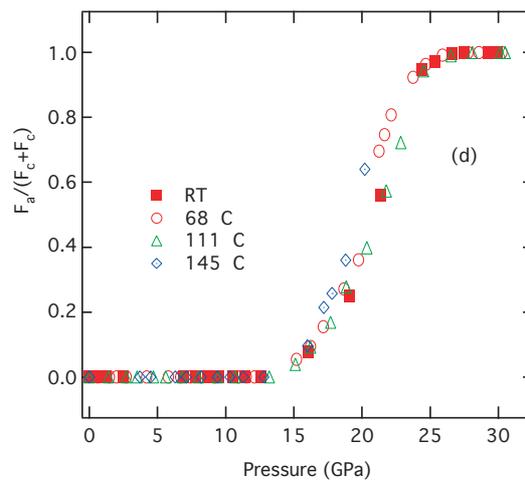


FIGURE 3: Fraction of the amorphous phase as a function of pressure: the amorphous phase starts to grow at 14 - 15 GPa with the material becoming completely amorphous at 25 GPa independent of temperature [5]

There are, however, substantial differences in the decompression behavior. At lower temperatures (room temperature to 110° C, the amorphous phase is stable upon decompression. At the same time, at 145 °C, i.e. just below the crystallization temperature, the amorphous phase is stable up to (or down to) rather low pressures but when the pressure is completely released the initial fcc phase is recovered as shown by the lower curve in Fig. 4.

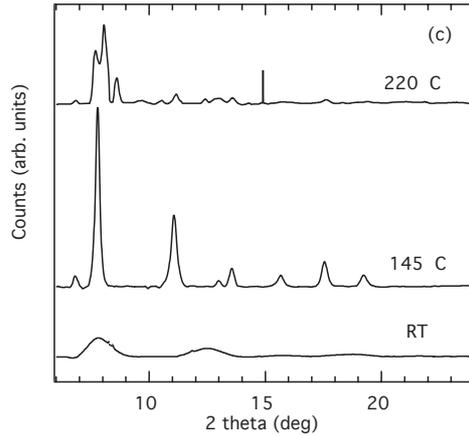


FIGURE 4: X-ray diffraction spectra of GST225 after compression and subsequent decompression at elevated temperatures. The corresponding temperatures are marked next to each curve

At temperatures close to the fcc-to-trigonal phase transition, the difference in behavior is even more spectacular. Up to 5 GPa, the fcc phase is stable but at higher pressures the trigonal phase starts to form. This process is followed by the appearance of numerous new peaks suggesting decomposition of the material. Upon decompression a trigonal form is obtained along with an additional phase (Fig. 4, upper curve) which may correspond to an orthorhombic high-pressure form of GeTe [].

To investigate changes on the atomic scale we also performed XAFS measurements (Fig. 5). Our results demonstrate Ge-Te bond shortening in the amorphous state similar to the case of laser-induced amorphisation. From this result we can suggest the the local structure of the two phases (around the Ge species at least) are similar [].

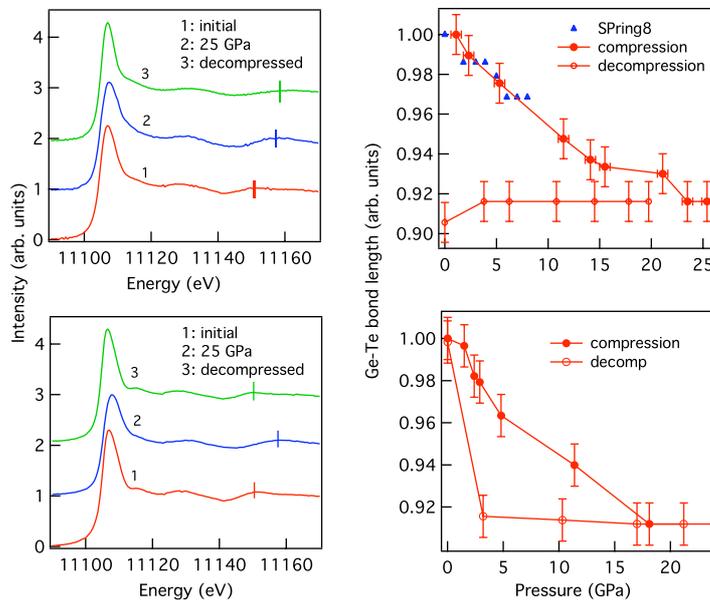


FIGURE 5: Variations of XAFS spectra of cubic GST225 at room temperature (upper left) and at 120 C (lower left) upon compression and decompression as well as the corresponding changes in the Ge-Te bond lengths (right-hand panels). Closed and open symbols refer to

the bond length changes upon compression and decompression, respectively. The vertical lines depict the error bars for the bond length determination. Triangles correspond to the results of the transmission measurements Ge K-edge EXAFS using a large multi-anvil press [6]

At the same time, the stable trigonal phase of GST(225) remains crystalline in the pressure range investigated. Considering the very similar bulk moduli of the materials studied this result suggests that vacancies present in the metastable cubic phase are crucial for the amorphisation.

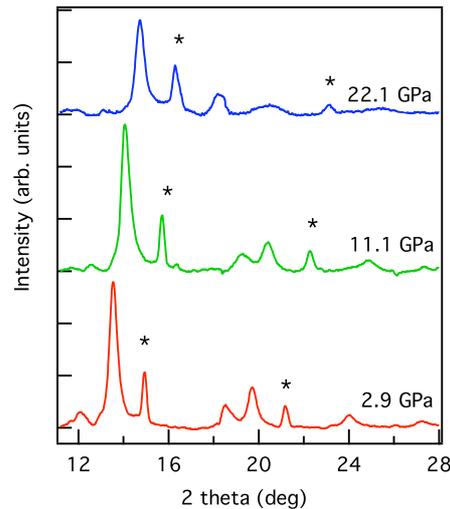


FIGURE 6: Pressure-induced changes of the XRD pattern of trigonal GST225 upon compression.

We would like now to address the question why GST becomes amorphous under pressure while the binary GeTe does not. We believe that the reason is two-fold. On the one hand, it may be that presence of the second constituent Sb_2Te_3 is needed. The different covalent radii of Ge and Sb give rise to a non-uniform strain distribution inside the material which may act as a driving force for the amorphization via nanophase separation that is often a driving force for pressure-induced amorphization in cases when the total volume of the decomposed phases is smaller than the volume of the starting material. The major reason, to our mind, is associated with presence of vacancies whose collapse allows for significant atomic motion and subsequent loss of the long-range order.

4. CONCLUSION

To conclude, we have observed that metastable cubic GST starts to amorphize at pressures above 10 GPa and becomes amorphous under hydrostatic pressure around 20 GPa at room temperature. While lack of information on the density of the liquid phase of GST does not allow us to conclude that the generated pressure is the major force that drives the bits into the amorphous state, the presented results clearly demonstrate that pressure is an important factor for the amorphisation process in a device structure and should be considered on the way for improvement of current and development of novel optical discs and electrical phase-change memories for future uses. It should also be stressed that nonhydrostatic conditions (such as shear deformation that are necessarily present in multilayered structures such as optical discs) can significantly decrease the pressure at which a phase change occurs.

The above discussion is also applicable to OUM and other types of phase-change memories when (whatever the inducing stimuli) a recorded amorphous bit is confined within a crystalline medium or vice versa.

REFERENCES

1. A.V. Kolobov et al., Phys. Rev. Lett., **97**, 035701 (2006)
2. A.V. Kolobov et al. Nature Mater., **3**, 703 (2004)
3. W. Welnic et al., Nature Mater., **5**, 56 (2006)
4. S. Shamoto et al., Appl. Phys. Lett. **86**, 081904 (2005)
5. A.V. kolobov et al., Appl Phys. Lett. **91**, 021911 (2007);
6. A.V. Kolobov et al., Appl. Phys. Lett. (in print)