

# Pressure induced phase transitions in $(\text{GeTe})_{1-x} - (\text{Sb}_2\text{Te}_3)_x$ nearby the rhombohedral to cubic transitions.

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## Introduction

Non-volatile phase change memory (PCM) data storage can successfully compete in speed and write-erase endurance with well-established flash memory devices and in the future they may serve as a replacement for DRAM in some applications. The PCM concept is based on the ability of an active component (a phase change material) to transform quickly and reversibly between amorphous and crystalline phases [1,2] (typically this transition occurs as a result of either electric current flowing through the active area of material or its irradiation by laser pulse), characterized by different electrical resistance and optical properties of a material. One of the most promising types among materials is a group of alloys along the GeTe-Sb<sub>2</sub>Te<sub>3</sub> tie-line.

The recorded bits in both optical and electronic data storages are amorphous (or crystalline) areas embedded in crystalline (or amorphous) surrounding. Since densities of the two phases are different, momentarily stresses are inevitable generated in the recorded bits and at the interfaces and are likely to play an important role in the device performance.

In Blu-Ray disk technology, GeTe-rich Ge-Sb-Te, namely Ge<sub>8</sub>Sb<sub>2</sub>Te<sub>11</sub>, exists in the rhombohedral lattice with concentration of Sb<sub>2</sub>Te<sub>3</sub> about 11% and 9% of vacancies in the cation sublattice and lays nearby the rhombohedral-to-cubic transition observed using the Bragg diffraction [3]. When temperature rises above 90°C, the rhombohedral phase turns to the high temperature cubic phase. It is important to stress that the concentration of vacancies in both phases should be the same and thus only the initial structural phase might play its role on the pressure induced phenomenon.

In order to better understand pressure-induced phase transitions, especially crystalline-to-amorphous in GeTe-rich Ge-Sb-Te alloys, we performed high-pressure phase transitions in rhombohedral Ge<sub>8</sub>Sb<sub>2</sub>Te<sub>11</sub> and cubic Ge<sub>4</sub>Sb<sub>2</sub>Te<sub>7</sub> containing 20% of Sb<sub>2</sub>Te<sub>3</sub> (close to the rhombohedral-to-cubic transition from the opposite site) at room temperature to disclose whether the admixture of 14% Sb<sub>2</sub>Te<sub>3</sub> in GeTe could be a trigger point for the pressure induced amorphisation (PIA) along GeTe-Sb<sub>2</sub>Te<sub>3</sub> tie-line and 2) and cubic Ge<sub>8</sub>Sb<sub>2</sub>Te<sub>11</sub> at 135°C to study the role of the initial state (rhombohedral and cubic) on pressure-induced phenomenon.

## Experimental Details

$\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  and  $\text{Ge}_4\text{Sb}_2\text{Te}_7$  (a cubic phase) samples were deposited on silicon substrates using magnetron sputtering and flash evaporation. The film thickness was about 500nm and consequently crystallised at 230°C for 1h under a low pressure Argon atmosphere to prevent sample oxidation.

We collected series of diffraction measurements from ambient pressure to 40 GPa with step of 2 GPa at room temperature and and 135°C at beam line ID09A at ESRF (Grenoble, France). The sample consisted of  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  and  $\text{Ge}_4\text{Sb}_2\text{Te}_7$  were placed in the gasket hole between the anvils of a diamond anvil cell. Helium and Neon gasses were used as pressure transmitting media to ensure the best possible hydrostatic conditions. A ruby photoluminescence as a pressure marker was used to determine the pressure in the cell. Debye-Scherrer diffraction images were collected with a monochromatic beam ( $\lambda = 0.4115\text{\AA}$ ) focused to ca. 20 x 20  $\mu\text{m}$  using a MAR345 online image plate reader. The pressure was increased or decreased in steps of ca. 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.

## Results and Discussion

The behavior of  $\text{Ge}_4\text{Sb}_2\text{Te}_7$  upon compression is shown in Fig. 1. The collapse of the cubic fcc phase starts to appear at 25 GPa and the amorphisation process continues until the crystalline fcc phase totally disappears at about 28 GPa. Upon decompression, the amorphous state remains until ambient conditions. The compression-decompression cycle in  $\text{Ge}_4\text{Sb}_2\text{Te}_7$  resembles the high pressure phase transitions in cubic  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  ( $\text{Ge}_1\text{Sb}_2\text{Te}_4$ ) which render amorphous at significantly lower pressures 16(12) GPa [4-7]. In contrast of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  ( $\text{Ge}_1\text{Sb}_2\text{Te}_4$ ), the pressure amorphised  $\text{Ge}_4\text{Sb}_2\text{Te}_7$  does not recrystallise into the bcc structure until 40 GPa, which was the maximum pressure that we could apply to our samples.

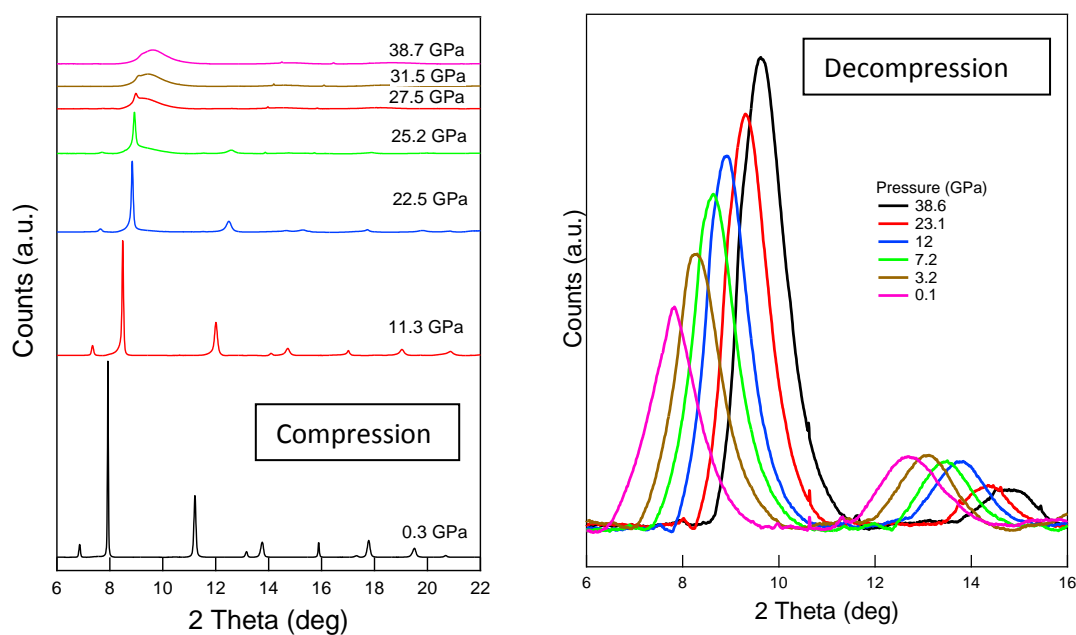


FIG. 1. The evolution of the synchrotron-based x-ray diffraction patterns of  $\text{Ge}_4\text{Sb}_2\text{Te}_7$  upon compression (left figure) and decompression (right figure) upon compression and decompression.

Low temperature  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  crystallises in the rhombohedral phase. Upon compression (see Fig. 2), the rhombohedral structure turns to the cubic phase at about 3.8 GPa and subsequently collapses into the amorphous phase at 32 GPa. The amorphous phase is stable upto 40 GPa without any signature of the bcc phase formation. Upon decompression, the amorphous phase reverts into the cubic phase between 9 to 6 GPa and remains stable until ambient environment. It seems that the admixture of 14%  $\text{Sb}_2\text{Te}_3$  in GeTe, the boundary between the existence of the rhombohedral and cubic phases at low temperature, does not strongly effect the pressure induced amorphisation phenomenon. It was found that the difference in pressure inducing the amorphisation in  $\text{Ge}_4\text{Sb}_2\text{Te}_7$  and  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  is  $\sim 4$  GPa. On the other hand, the  $\text{Sb}_2\text{Te}_3$  content in GeTe equals to 14% seems to be the maximum concentration which ensures the spontaneous recrystallisation of the pressure amorphised phase when decompressed. Thus,  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  could be a suitable candidate for reversible crystal to amorphous to crystal cycling using high hydrostatic pressure conditions.

The high temperature modification of  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  can be found in the cubic structure. Under elevated pressure, the cubic phase amorphises at about 30 GPa which is approximately 2 GPa lower than in the case of its low temperature modification (see Fig. 3). The result indicates that PIA in  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  might be thermally activated ( $\sim 2$  GPa difference). We believe that the thermal disorder could reduce the pressure to transform a crystal to an amorphous state. Upon decompression, the cubic phase was restarted between 11 and 3 GPa.

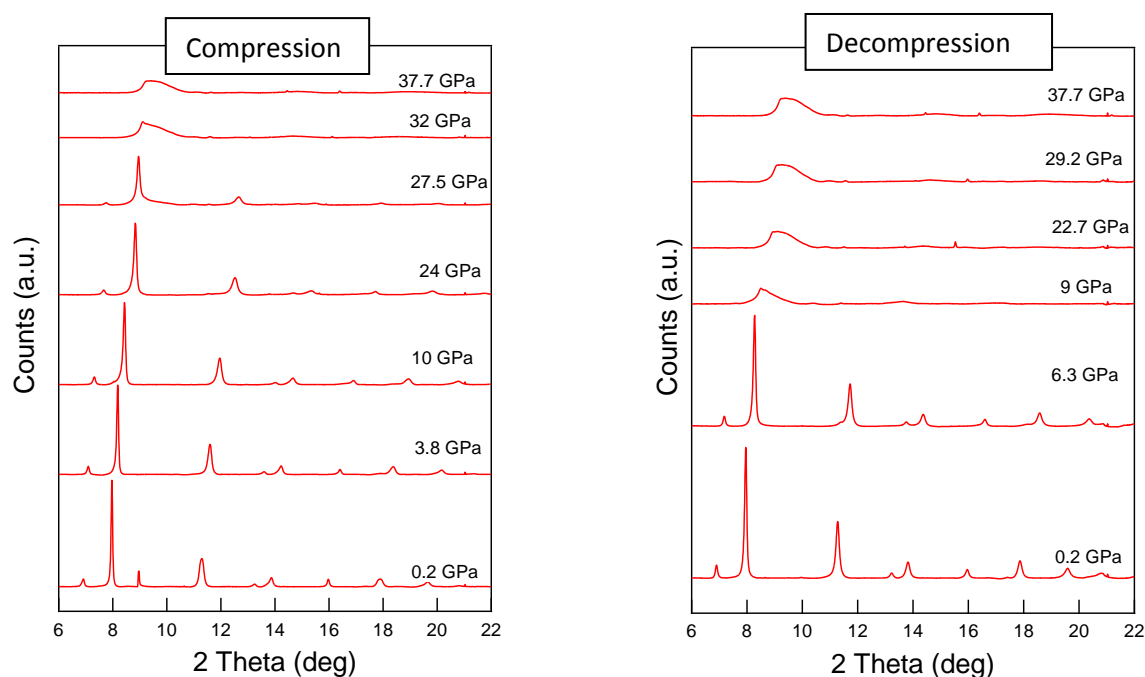


FIG. 2. The evolution of the synchrotron-based x-ray diffraction patterns of  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  upon compression (left figure) and decompression (right figure) at room conditions.

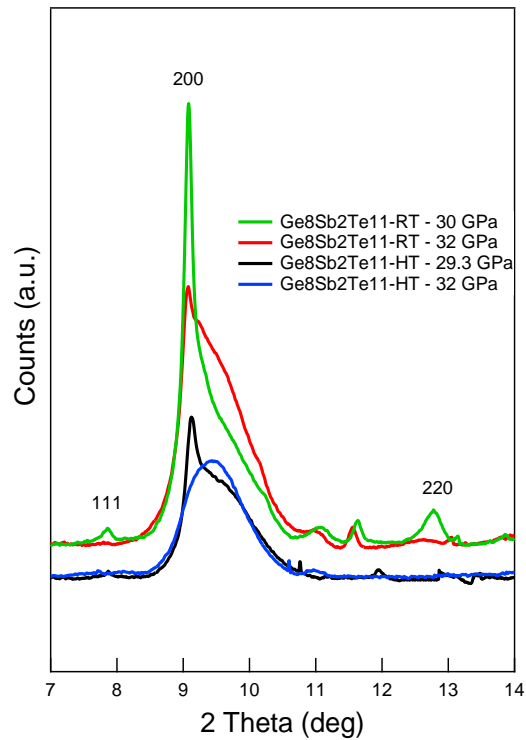


FIG. 3. The evolution of the pressure induced amorphisation in  $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$  at room temperature (RT) and  $135^\circ\text{C}$  (HT).

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