# Structural Basis for Fast Phase Change of DVD-RAM

The development of fast phase-change materials in the last century was accomplished as result of the landmark studies on GeTe and Au-Ge-Sn-Te compounds in a single-phase structure by Chen *et al.* [1] and Yamada *et al.* [2], respectively.  They reported that these materials show a high phase-stability of the amorphous phase and a very short crystallization time.  These approaches led the way to the development of new phase-change rewritable materials and to the discovery, in 1987, of the GeTe-$Sb_2Te_3$ single-phase material by Yamada *et al.* [3].  The pseudobinary compound 2GeTe-$Sb_2Te_3$ ($Ge_2Sb_2Te_5$) is one of the well-established mother materials for commercial DVD-RAM (digital versatile disc-random access memory) devices that utilize the crystal-liquid-amorphous (record) and amorphous-crystal (erase) phase change in chalcogenide materials.  In order to develop faster phase-change materials, it is necessary to understand the structural origins of the phase change, especially for the 3D structure of the amorphous phase in the amorphous to crystal phase changes.  Recently, Kolobov *et al.* investigated the local coordination around the Ge, Sb, and Te atoms in both the crystal and the amorphous phases of $Ge_2Sb_2Te_5$ by means of extended X-ray absorption fine-structure spectroscopy (EXAFS).  They ascribed the crystal-amorphous/amorphous-crystal phase change in terms of the umbrella-flip of the Ge atoms from the octahedral site to the tetrahedral site, and concluded that the transformation between the two sites is the reason for the fast optical switching of the DVD-RAM [4].
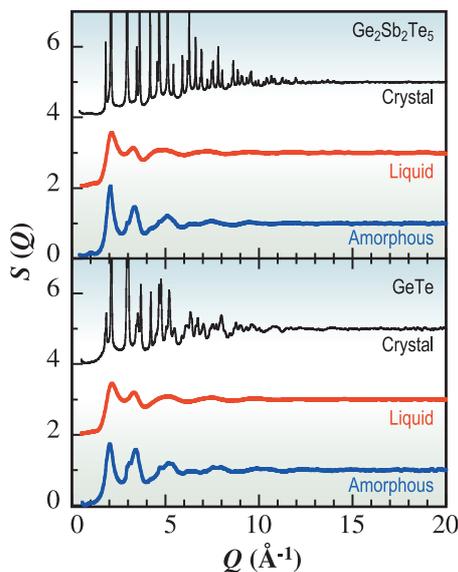
However, the proposed model based on EXAFS data reveals only the local structure of the amorphous phase; hence, it is necessary to analyze the large-scale 3D structure of the amorphous phase.  In this study, we derived the 3D atomic configuration of amorphous $Ge_2Sb_2Te_5$ (a-$Ge_2Sb_2Te_5$, crystallization speed: 20 ns) and amorphous GeTe a-GeTe, crystallization speed: 100 ns) by reverse Monte Carlo (RMC) computer simulation with synchrotron radiation X-ray diffraction data [5].

The high-energy X-ray diffraction experiments were carried out at the SPring-8 high-energy X-ray diffraction beamline **BL04B2** and powder diffraction beamline **BL02B2**.  The measured data were analyzed by both Rietveld analysis and RMC simulation.

Figure 1 shows the measured structure factors $S(Q)$.  The diffraction patterns of $Ge_2Sb_2Te_5$ and GeTe crystals consist of sharp Bragg reflections, indicating long-range periodicity in the atomic arrangement.  On the other hand, the diffraction patterns of $Ge_2Sb_2Te_5$ (953 K) and GeTe (1073 K) liquids show a typical halo pattern peculiar to non-crystalline materials, reflecting the lack of long-range periodicity.  These diffraction patterns show a highly disordered state (liquid state) that both $Ge_2Sb_2Te_5$ and GeTe must undergo during a recording process (crystal-amorphous phase change) by a laser-heated melt-quench process.

In order to characterize the short-range structural units, we investigated the bond angle distributions within the first coordination shell of $g_{ij}(r)$.  Figure 2 shows the distributions in a-$Ge_2Sb_2Te_5$ and a-GeTe with the typical bond angle distribution, O-Si-O of regular tetrahedron, $SiO_4$, in amorphous $SiO_2$.  Te-Ge(Sb)-Te and Ge(Sb)-Te-Ge(Sb) in a-$Ge_2Sb_2Te_5$ exhibit a peak at around 90°, which, surprisingly, consists of the angle in the corresponding crystal phase and is different from the typical bond angle, 109.4°, of O-Si-O.  Te-Ge-Te in a-GeTe exhibits a
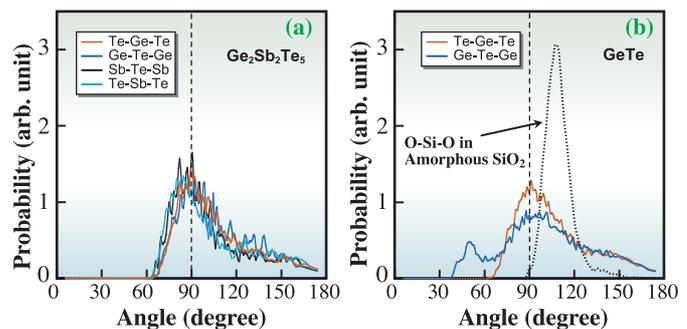


Fig. 1.  Total structure factors $S(Q)$ of crystal (300 K), liquid (953 K), and amorphous $Ge_2Sb_2Te_5$ (300 K) and crystal (300 K), liquid (1073 K), and amorphous GeTe.



Fig. 2.  Bond angle distributions in a-$Ge_2Sb_2Te_5$ and a-GeTe.  Dotted lines represent the distribution of O-Si-O of regular tetrahedra in amorphous $SiO_2$.
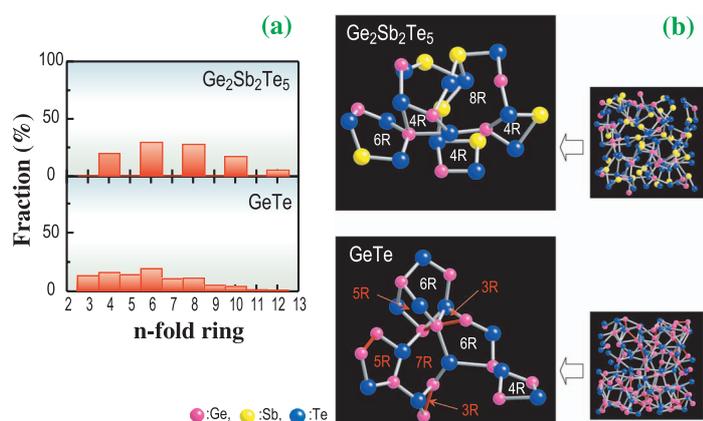
Fig. 3. Ring size distributions in a-Ge₂Sb₂Te₅ and a-GeTe **(a)**. The 16 Å × 16 Å × 16 Å atomic configurations and enlarged framework atomic configurations of a-Ge₂Sb₂Te₅ and a-GeTe obtained from the RMC snapshot **(b)**.

similar bond angle distribution, but Ge-Te-Ge shows peaks at around 90° and 50° because of the formation of Ge-Ge homopolar bonds. Therefore, it is suggested that a-Ge₂Sb₂Te₅ possesses a crystal-like bond angle order, whereas a-GeTe loses such an order upon the formation of Ge-Ge bond. The total coordination number around Ge (Sb) derived from the RMC model is estimated at 3.7 (3.0) for a-Ge₂Sb₂Te₅ and 4.1 around the Ge for a-GeTe. Therefore it is suggested that dominant short-range structural units are GeTe₄ and SbTe₃ for a- Ge₂Sb₂Te₅, and GeTe₄ and GeTe₃Ge for a-GeTe.

The ring statistics for the amorphous and crystal Ge₂Sb₂Te₅ and GeTe were calculated up to the 12-fold ring, as shown in Fig. 3(a). It is remarkable that a-Ge₂Sb₂Te₅ can be regarded as a "even-numbered ring structure," because the ring statistics is dominated by 4- and 6-fold rings analogous to the crystal phase. On the other hand, we find that a-GeTe has various sizes (both odd- and even-numbered) of rings. These

differences in the network of the ring structure are clearly visible in 3D atomic configurations obtained by RMC simulation, as shown in Fig. 3(b).

On the basis of the comparison of the ring statistics, the mechanisms of fast crystal-liquid-amorphous (record) and amorphous-crystal (erase) phase changes in Ge₂Sb₂Te₅ are proposed, as shown by the schematic presentation in Fig. 4. In the crystal-liquid phase-change process (stage I), the atomic configuration in the crystal phase is disarranged by laser heating and melted in liquid, where there is no significant structural difference between Ge₂Sb₂Te₅ and GeTe (see also Fig. 1).

However, in the liquid-amorphous phase-change process (stage II), only even-numbered rings are constructed in a-Ge₂Sb₂Te₅. In the amorphous-crystal phase-change process (stage III), a-Ge₂Sb₂Te₅ transforms to the crystal phase via the transformation of only the large even-numbered (8, 10, 12-fold) rings into the crystal structure (4- and 6-fold rings). On the other hand, a-GeTe exhibits various sizes (both odd- and even-numbered) of rings in stage II. Therefore, the recombination of the various-size rings is required in stage III. Thus the construction of odd-numbered rings in a-GeTe disturbs the fast crystallization of the amorphous phase, and it is worth mentioning that the addition of Sb₂Te₃ to GeTe can effectively prevent the formation of Ge-Ge bonds in a-Ge₂Sb₂Te₅.

In conclusion, we found that the ring statistics of amorphous Ge₂Sb₂Te₅ is dominated by 4- and 6-fold rings analogous to the crystal phase, by means of RMC analysis. We believe such unusual ring statistics of amorphous Ge₂Sb₂Te₅ to be the key in the fast crystallization speed of the material.

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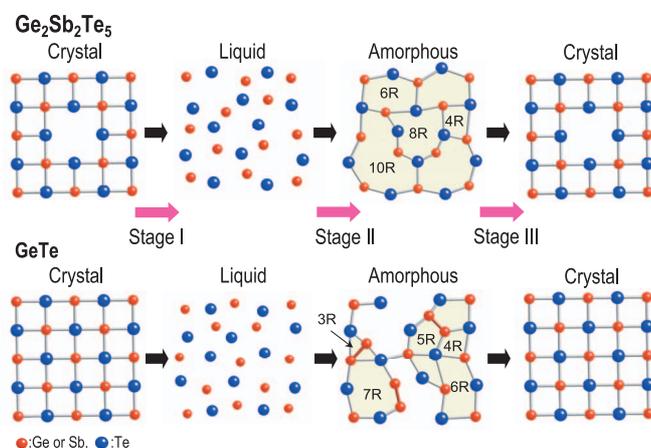
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Fig. 4. Schematic presentation of possible ring size transformation in crystal-liquid-amorphous phase change (record) and amorphous-crystal phase change (erase) in Ge₂Sb₂Te₅ and GeTe. Stages I and II: recording process, stage III: erasing process.

**References**

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