Structural basis for fast phase change of DVD-RAM

-Topological order in the amorphous phase-

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ABSTRACT

The DVD-RAM (digital versatile disc-random access memory), which utilizes the melt-quenching (amorphizing for record) and annealing (crystallization for erase) processes of chalcogenide materials. It is well known that $Ge_2Sb_2Te_5$ is one of the well-established commercial media. In this study, we revealed the 3-dimensional atomic configuration of amorphous $Ge_2Sb_2Te_5$ and GeTe by reverse Monte Carlo simulation with synchrotron-radiation high-energy x-ray

diffraction data. The RMC models suggested that amorphous $Ge_2Sb_2Te_5$ can be regarded as "even numbered-rings structure", because the ring statistics is dominated by 4- and 6-fold rings analogous to the crystal phase. On the other hand, the formation of Ge-Ge homopolar bonds in amorphous GeTe constructs both odd- and even-numbered rings and it is worth mentioning that the addition of Sb_2Te_3 to GeTe can effectively prevent the formation of Ge-Ge bonds in amorphous $Ge_2Sb_2Te_5$. We believe such a topological order in amorphous $Ge_2Sb_2Te_5$ manifested by ring statistics is the key for the fast crystallization speed of the material.

Key words: Phase-change materials, Chalcogenide materials, High-energy x-ray diffraction, Reverse Monte Carlo modelling.

1. INTRODUCTION

A new era in phase-change materials was opened by Chen et al.'s study on GeTe compound [1] and Yamada and co-worker's study on Au-Ge-Sn-Te in a single-phase structure [2]. 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 devices, since the phase change between the crystal phase and the amorphous phase completes within 20 nsec [4], whereas GeTe requires 100 nsec [1]. In order to develop faster phase-change materials, it is necessary to understand the structural origins of the phase change, especially for the 3-dimensional structure of the amorphous phase in the amorphous to crystal phase changes.

Yamada and co-worker revealed a NaCl-type structure of the laser-crystallized $Ge_2Sb_2Te_5$ using the Rietveld analysis on the synchrotron-radiation x-ray diffraction data [5]. The lattice constant is 6.02 Å. The $4(a)$ sites are wholly occupied only by the Te atoms, while the $4(b)$ sites are randomly occupied by the Ge and Sb atoms. There exists 20 % vacancy at the $4(b)$ site, which may be related with the large atomic displacement factor of the Ge atom [6]. On the other hand, GeTe crystal exhibits trigonal structure where both Ge and Te occupy $4(a)$ site without vacancy [7].

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 [8]. Furthermore this model was slightly modified and extended to spinel structure based on *ab initio* calculation by Welnic et al [9]. 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 3-dimensional structure of the amorphous phase based on experimental data. Moreover it is well known that crystal-amorphous phase change is accomplished by a melt-quenching process, therefore, it is necessary to analyze the amorphous structure in a crystal-liquid-amorphous and a amorphous-crystal phase-change process for getting deep insights on fast phase change. Accordingly, we derived the 3-dimensional atomic configuration of amorphous $Ge_2Sb_2Te_5$ (a-$Ge_2Sb_2Te_5$) and amorphous GeTe (a-GeTe) by reverse Monte Carlo (RMC) computer simulation [10] with synchrotron radiation x-ray diffraction data with special focus on the relationship between the speed of phase change and the atomic configuration of the amorphous phase [11]. In this paper, the structure of a-$Ge_2Sb_2Te_5$ and the structural origin of the fast crystallization speed are described in detail.

2. EXPERIMENTS

The specimen for high-energy x-ray diffraction experiment was made by laminating organic film sheet on a glass disk with a diameter of 120 mm and sputtering to form the recording film with a thickness of 200 - 500 nm. The organic film sheet was peeled off from the glass disk and specimen was manually scratching off from the glass substrate using a spatula. The composition of the sample was examined by inductively coupled plasma atomic emission spectrometry.

The high-energy x-ray diffraction experiments at room temperature were carried out at the SPring-8 powder diffraction beamline BL02B2 [12] and the high-energy x-ray diffraction beamline BL04B2 [13,14]. The diffraction patterns of powder sample in a thin walled (10 μm) tube of 0.5 mm diameter (supplier: GLAS Müller, D-13503 Berlin) were measured in transmission geometry. The experiments on liquids were carried out at BL04B2 using a high-temperature furnace. The diffraction patterns of liquid sample in a silica glass tube of 2.0 mm diameter and 0.5 mm wall thickness were measured at 653 K ($Ge_2Sb_2Te_5$) and 1073 K (GeTe), respectively. The collected data were corrected using standard programs. The absorption coefficients [15], incoherent scattering functions [16], and atomic scattering factors [17] were used for the corrections and normalization. The corrected data were normalized to Faber-Ziman [18] total structure factor $S(Q)$.

The RMC simulation was performed on an ensemble of 3686 and 4096 particles for $Ge_2Sb_2Te_5$ and GeTe, respectively, starting with the NaCl-type configuration. Throughout the RMC simulation, the constraint of closest atom-atom approach was applied so as to avoid the appearance of unphysical spikes in the partial pair-distribution functions. The atomic number density of a-$Ge_2Sb_2Te_5$ and a-GeTe is chosen to be 0.0315 and 0.0337 $Å^{-3}$, respectively. The density of amorphous phase is consistent with the reported data [19,20].

3. RESULTS & DISCUSSION

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. Although the $S(Q)$ of a-$Ge_2Sb_2Te_5$ is similar to that of a-GeTe, the sharpness of the first diffraction peak observed at around $Q=2$ $Å^{-1}$ in $S(Q)$ of a-$Ge_2Sb_2Te_5$ is larger than that in a-GeTe, suggesting a-$Ge_2Sb_2Te_5$ exhibits more ordered structure than a-GeTe.

Figure 2 shows the total correlation functions $T(r)$ obtained by Fourier transformation of $S(Q)$. The first peak observed at around 3.0 Å in the $T(r)$ of both crystals is assigned to the Ge(Sb)-Te correlations. It is remarkable that the GeTe crystal exhibits two Ge-Te correlation lengths (2.8 and 3.2 Å), whereas $Ge_2Sb_2Te_5$

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. Solid lines and dashed lines represent the experimental data and the result of the RMC simulation data, respectively.

Fig. 2. Total correlation functions, $T(r)$, 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.

crystal shows a relatively sharp peak composed of the Ge-Te and Sb-Te correlations (3.0 Å). Thus, one may notice there is significant shrinkage of the Ge(Sb)-Te correlation distance at the phase change from the crystal phase (3.0 Å)
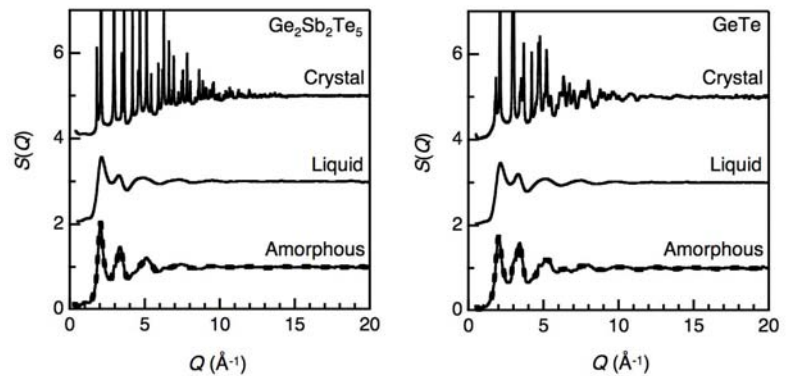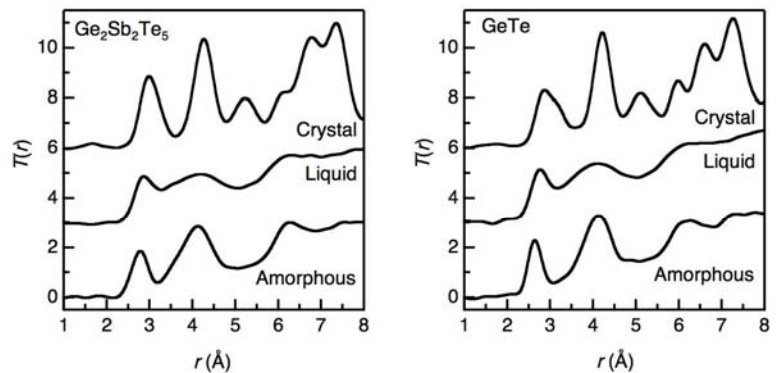
to the amorphous phase (2.78 Å). The variations of the atomic distance and the peak intensity can be ascribed to the reduction of the coordination number of the Te atom around the Ge (Sb) atom.

It is worth mentioning that the peak corresponding to the Te-Te correlation distance observed at around 4.2 Å in both $Ge_2Sb_2Te_5$ and GeTe becomes broader in the liquid phases and sharper again in the amorphous phase. In addition, a peak observed at around 5 Å, which corresponds to the diagonal length in a cubic cell, disappears in both liquid and amorphous phase. It is suggested from these features that both crystals lose the local and long-range atomic orders in liquid phase and get some specific atomic orders in the amorphous phase again. These observations seem to contradict with the "umbrella

Fig. 3. The partial pair-distribution functions $g_{ij}(r)$ of a-$Ge_2Sb_2Te_5$ and a-GeTe. Black lines: a-GeTe, red lines: a-$Ge_2Sb_2Te_5$ (non-homopolar bond model), blue lines: a-$Ge_2Sb_2Te_5$ (homopolar bond model).

model" proposed by Kolobov et al., in which rigid Te-sublattice is postulated [8]. Hence it is necessary to envisage the small displacement and atomic diffusion of not only Ge atoms but also all atoms, which may make it possible to realize the fast-phase change of DVD-RAM. In addition, it should be mentioned that GeTe shows a significant change of the Ge-Te correlation distance and the peak height at the phase change process from the liquid phase (2.77 Å) to the amorphous phase (2.65 Å), while $Ge_2Sb_2Te_5$ shows a relatively small change. Maeda and Wakagi discovered the Ge-Ge homopolar bonds at 2.48 Å in a-GeTe, which disappear during amorphous-crystal phase change process [21]. Pickart et al. performed neutron diffraction experiment on a-GeTe [20] and found the first peak at 2.60 Å in real-space function, which is smaller than that of 2.65 Å of our x-ray diffraction data. The difference in appearance of the Ge-Ge homopolar bonds in between neutron and x-ray experiments is explained by the difference of the weighting factors of Ge-Ge and Ge-Te for neutrons and x-rays. Thus, the x-ray and neutron diffraction and EXAFS data of GeTe suggest the existence of Ge-Ge homopolar bonds in a-GeTe. However Kolobov et al. does not mention about the formation of such a homopolar bond in a-$Ge_2Sb_2Te_5$ based on EXAFS data [8]. Unfortunately it is difficult to confirm the formation of homopolar bonds (Ge-Ge, Ge-Sb, Sb-Sb) in a-$Ge_2Sb_2Te_5$ from our x-ray diffraction data.

The total structure factors $S(Q)$ of a-$Ge_2Sb_2Te_5$ and a-GeTe derived from the RMC model are shown in Fig. 1 as a dashed line. It is confirmed that the RMC models are consistent with experimental data. The partial pair-distribution functions $g_{ij}(r)$ of a-$Ge_2Sb_2Te_5$ and a-GeTe are shown in Fig. 3 with a red line and black line, respectively. It is worth mentioning that the first peak in $g_{ij}(r)$ of Ge-Te and Sb-Te is sharp but skewed towards the high-r side, indicating a distribution of Ge-Te and Sb-Te distances from 2.4 to 3.4 Å due to highly distorted polyhedra.

In order to characterize the structural units, we investigated the bond angle distributions within the first coordination shell of the $g_{ij}(r)$ as shown in Fig. 4. Te-
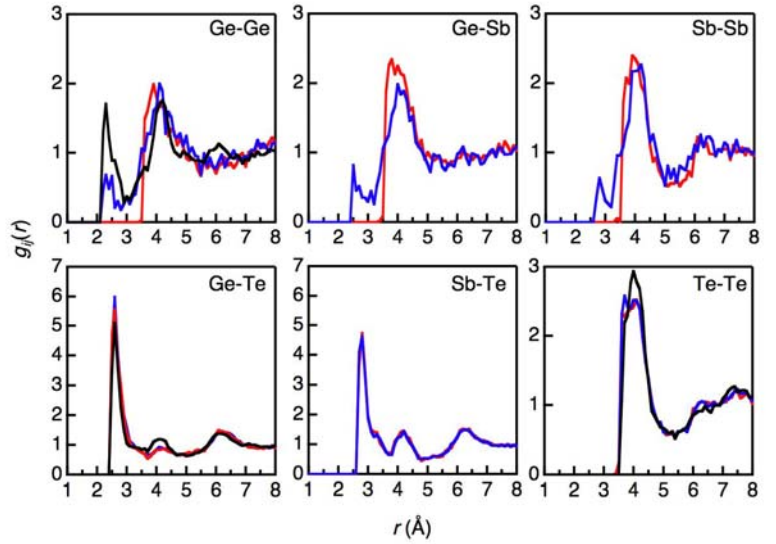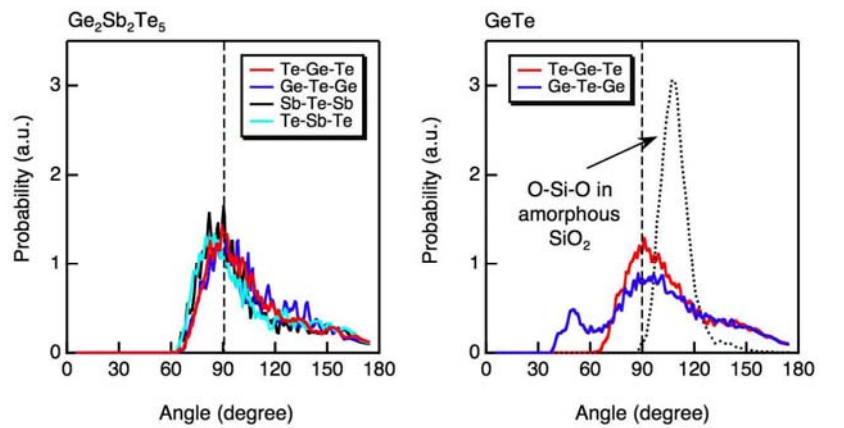

Fig. 4. Bond angle distribution in a-$Ge_2Sb_2Te_5$ and a-GeTe. Dotted lines represent the distribution of O-Si-O of regular tetrahedra in amorphous SiO_2 calculated from the RMC model [22].

Ge(Sb)-Te and Ge(Sb)-Te-Ge(Sb) in a-$Ge_2Sb_2Te_5$ exhibit a peak at around 90°, which surprisingly consists with the angle in the corresponding crystal phase and are different from the typical bond angle, 109.4° of the O-Si-O of regular tetrahedra, SiO_4, in amorphous SiO_2 [22]. Te-Ge-Te in a-GeTe exhibits similar bond angle distribution, but Ge-Te-Ge shows peaks at around 90° and 50° due to the formation of Ge-Ge homopolar bond. Therefore it is suggested that a-$Ge_2Sb_2Te_5$ possesses crystal-like bond angle order, whereas a-GeTe loses such an order by the formation of Ge-Ge bond. The total coordination number around the Ge(Sb) derived from the RMC model is estimated to be 3.7 (3.0) for a-$Ge_2Sb_2Te_5$

Fig. 5. Ring size distribution in (a) $Ge_2Sb_2Te_5$ (b) GeTe, and (c) a-$Ge_2Sb_2Te_5$ with Ge-Ge, Ge-Sb, Sb-Sb homopolar bonds.

and 4.1 for a-GeTe. Therefore it is suggested that dominant short-range structural units are $GeTe_4$ and $SbTe_3$ for a-$Ge_2Sb_2Te_5$, and $GeTe_4$ and $GeTe_3Ge$ for a-GeTe. The coordination number of the Ge(Sb) atom around the Te atom is estimated to be 1.5 (1.2) in a-$Ge_2Sb_2Te_5$ and 3.1 in a-GeTe. Thus the estimated coordination number (2.7) around the Te atom in a-$Ge_2Sb_2Te_5$ is consistent with that in the Olson's argument [23], which insists that the coordination number should be about three with taking into account of only the Ge-Te and Sb-Te bonds.
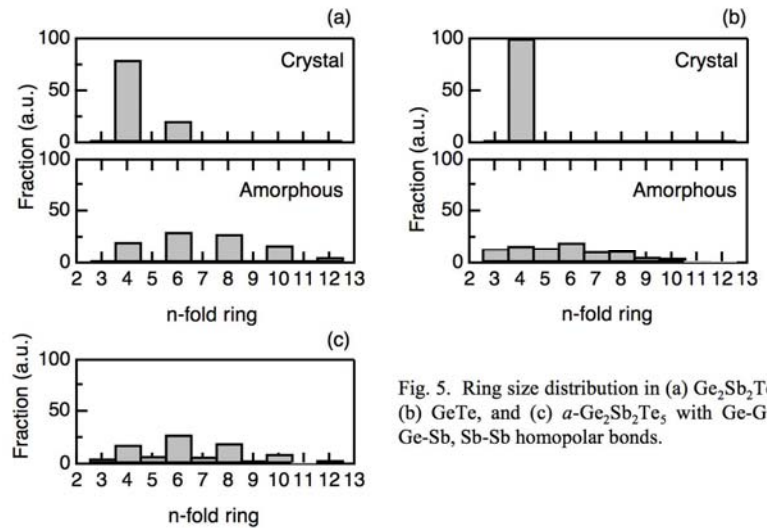
In order to obtain the insights on the relationship between the speed of phase change and the atomic configuration, the ring statistics in both crystal and amorphous phase for $Ge_2Sb_2Te_5$ and GeTe were calculated up to 12-fold ring, as shown in Fig. 5 (a) and (b), respectively. In the calculation, we defined that GeTe crystal has only 4-fold ring. In the case of $Ge_2Sb_2Te_5$ crystal, 20% of total number of vacancies in Ge/Sb mixing sites produces about 20 % of 6-fold ring. It is remarkable that the structure of a-$Ge_2Sb_2Te_5$ 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 due to the formation of Ge-Ge homopolar bonds. These differences in the ring interconnection structures are clearly visible in 3-dimensional atomic configurations obtained from the RMC simulation, as shown in Fig. 6. Recently Baker et al. reported that the formation of the Ge-Ge homopolar bond in a-$Ge_2Sb_2Te_5$ based on EXAFS data [24,25]. Although it is difficult to estimate the fraction of the Ge-Ge homopolar bonds due to the small weighting factor for x-rays, the RMC modelling with/without homopolar bonds (Ge-Ge, Ge-Sb, Sb-Sb) in a-$Ge_2Sb_2Te_5$ was performed. The RMC model with homopolar bonds exhibited good agreement with experimental data within experimental errors. The calculated $g_{ij}(r)$ and the ring statistics are shown in Fig. 3 as blue lines and Fig. 5(c), respectively. As can be seen in Fig. 3, the small peaks corresponding to the homopolar bond are observed in $g_{ij}(r)$ for the Ge-Ge, Ge-Sb, and Sb-Sb, but the fraction of Ge-Ge homopolar bonds in a-$Ge_2Sb_2Te_5$ is smaller than that in a-GeTe. Recent other RMC modelling using a combination of diffraction and EXAFS data suggests that the formation of homopolar bonds [26,27], too. However even-numbered rings are still dominant in a-$Ge_2Sb_2Te_5$ under
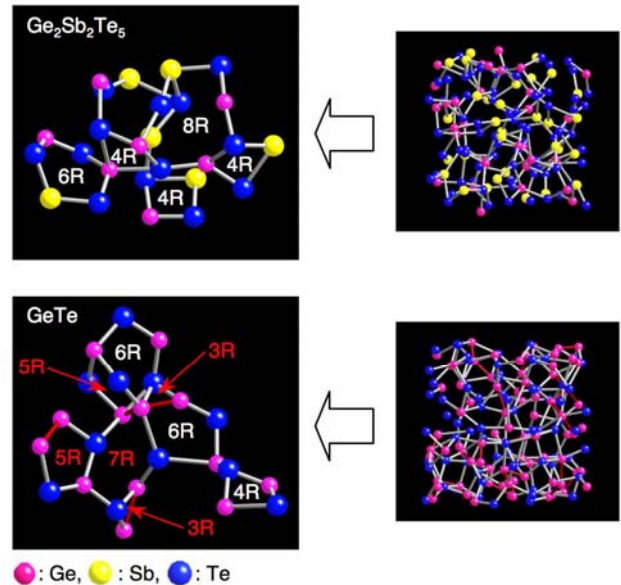

Fig. 6. A 16 Å x 16 Å x 16 Å atomic configuration and enlarged framework atomic configuration of a-$Ge_2Sb_2Te_5$ and a-GeTe obtained from the RMC snapshot (b). The Ge(Sb)-Te and Ge-Ge bonds shorter than 3.4 Å and 3.0 Å are indicated by the sticks, respectively. The red-colored bond represents the Ge-Ge bond.

the formation of homopolar bonds, suggesting the addition of Sb_2Te_3 to GeTe can effectively prevent the formation of Ge-Ge bonds in a-$Ge_2Sb_2Te_5$.

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 $Ge_2Sb_2Te_5$ are proposed, as shown by the schematic presentation in Fig. 7. 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 $Ge_2Sb_2Te_5$ and GeTe (see also Fig. 1). However, in
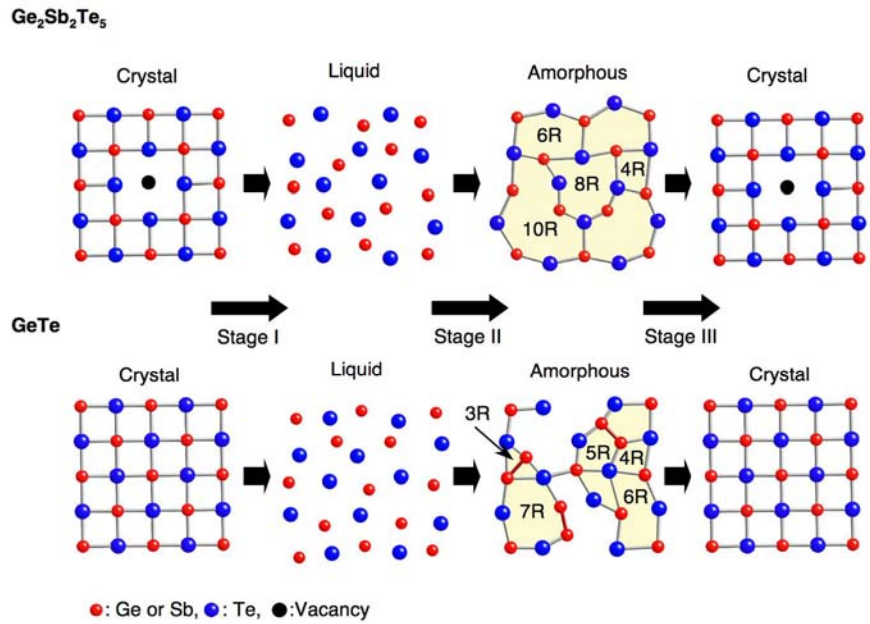

Fig. 7. A schematic presentation for the possible ring size transformation in crystal-liquid-amorphous phase change (record) and amorphous-crystal phase change (erase) in $Ge_2Sb_2Te_5$ and GeTe. The red-colored bond represents the Ge-Ge bond. Stage I and II: recording process, stage III: erasing process.

the liquid-amorphous phase-change process (stage II), only even-numbered rings are constructed in a-$Ge_2Sb_2Te_5$. In the amorphous-crystal phase-change process (stage III), a-$Ge_2Sb_2Te_5$ 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. Such a topological order in a-$Ge_2Sb_2Te_5$ manifested by ring statistics is generally incompatible with disordered structure in amorphous materials. Amorphous materials do not usually exhibit such a characteristic topological order and show a broad feature as seen in Fig. 5(b) for a-GeTe due to the structural disorder [28, 29]

4. CONCLUSION

The 3-dimensional atomic configurations of a-$Ge_2Sb_2Te_5$ and a-GeTe were derived by reverse Monte Carlo simulation with synchrotron-radiation high-energy x-ray diffraction data. We found that the ring statistics of a-$Ge_2Sb_2Te_5$ is dominated by 4- and 6-fold rings analogous to those of the crystal phase. It is suggested that the addition of Sb_2Te_3 to GeTe can effectively prevent the formation of Ge-Ge bonds in a-$Ge_2Sb_2Te_5$. The origin of the fast phase change in DVD-RAM is a material developer's question for many years and we believe that "even numbered-rings structure" in a-$Ge_2Sb_2Te_5$ is an essential feature for fast phase-change materials. Furthermore it is worth mentioning that these topological findings can be obtained from structural modelling with the RMC method, since the diffraction data does not exhibit any structural similarity between amorphous and crystal in real space. We are confident that the results of this study will provide important directions in the future design of fast phase-change materials.

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