

Structural analysis of GeSbTeSe phase-change materials

Toshiyuki Matsunaga,^{a, e} Rie Kojima,^b Noboru Yamada,^{b, e} Kouichi Kifune,^c
Yoshiki Kubota,^d Shinji Kohara^e and Masaki Takata^{e, f, g}

^a Materials Science and Analysis Technology Center, Panasonic Corporation
3-1-1 Yagumo-Nakamachi, Moriguchi, Osaka 570-8501, Japan
Correspondence e-mail: matsunaga.toshiyuki@jp.panasonic.com

^b Digital & Network Technology Development Center, Panasonic Corporation
3-1-1 Yagumo-Nakamachi, Moriguchi, Osaka 570-8501, Japan

^c Faculty of Liberal Arts and Sciences, Osaka Prefecture University
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

^d Graduate School of Science, Osaka Prefecture University
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan

^e CREST, Japan Science and Technology Agency

4-1-8 Honmachi, Kawaguchi, Saitama 332-0012, Japan

^f RIKEN SPring-8 Center

1-1-1, Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148 Japan

^g Department of Advanced Materials Science, The University of Tokyo
5-1-5, Kashiwanoha, Kashiwa, Chiba 227-8561 Japan

ABSTRACT

Generally, the superior rewritable phase-change recording material has to possess the following characteristics:

- (1) records can be written very fast,
- (2) records can be retained stably for extended periods of several decades,
- (3) records can be rewritten up to $10^4 \sim 10^6$ times, and
- (4) they show sufficient optical and electric changes between the two phases.

The first and second characteristics are the two extremes, apparently incompatible with each other; however, it is well-known that the GeTe-Sb₂Te₃ (GST) materials possess both, showing superior capabilities for high-speed rewritable and non-volatile memories. By using the films of these materials, DVDs and Blu-ray disks have been already commercialized. The aim of this paper is, however, to discuss the necessity of phase-change materials having higher amorphous stabilities for future ultra high-density phase-change memories. With increasing the recording density of phase-change media, the mark size must become smaller and smaller, which will be down to 10 nm or less in 500GB - 1TB disks. It is still required that even such tiny amorphous marks consisting of fewer atoms keep on retaining their phases stably for several decades or for a century under usual life environment. It is easily expected, however, that the replacement of Te by elements with stronger covalent bonding nature, for instance, S or Se, in the GST materials may provide those materials higher amorphous stabilities. To develop future higher-density memories, as a first step for this purpose, we examined the structures and their temperature dependences of amorphous and crystalline Ge₂Sb₂(Se_xTe_{1-x})₅ by using synchrotron radiation facilities.

Key words: phase-change memory, Ge₂Sb₂Se₅, XRD, EXAFS, atomic configuration, endurance

1. INTRODUCTION

In phase-change optical disks, a large capacity data can be recorded by forming the high-density amorphous marks on the recording film. The most widely used recording material for optical disks today is GeTe-Sb₂Te₃ (GST) pseudo-

binary materials [1], [2]. This is because these materials have four characteristics essential for rewritable data storage: (1) records can be rewritten very fast, and (2) records can be retained stably for extended periods of several decades, (3) records can be rewritten up to $10^4 \sim 10^6$ times, and (4) they show sufficient optical and electric changes between the two phases. The first and second characteristics are the two extremes, apparently incompatible with each other; however, these GST materials possess both, showing superior capabilities for high-speed rewritable and non-volatile memories. To meet these requirements, Blu-ray discs with a dual-layer structure, on which as much as 50 GB of information can be recorded by adopting these materials, have been placed on the market. The market strongly demands, however, that higher and higher density recording media such as 1TB \sim 1PB disk are realized. With increasing the density, the portion necessary for each memory bit in the recording layer becomes smaller and smaller; which means that the memory bits become more susceptible to their surroundings to easily transform into a crystalline phase. We will have to then find means to obtain not only the faster rewrite speed but also the amorphous stability, to realize future ultra-high-density phase-change memories. It is well-known that Se or S forms stronger covalent bond than Te, which makes us expect that replacement of Te in GST materials by the chalcogens with smaller atomic numbers would give stabilities to their amorphous phases. In this study, structures of some $\text{Ge}_2\text{Sb}_2(\text{Se}_x\text{Te}_{1-x})_5$ materials were investigated by performing the XRD (x-ray diffraction) and EXAFS (extended x-ray absorption fine structure) measurements and analyses. As expected, the XRD measurements showed that $\text{Ge}_2\text{Sb}_2\text{Se}_5$ kept on retaining its amorphous phase up to around 560 K, which is much higher than the transition temperature, 400K, to the crystalline phase of $\text{Ge}_2\text{Sb}_2\text{Te}_5$. In addition, with increasing the temperature, the amorphous phase, without showing the intermediate rock-salt structure, turned into a crystalline phase with a very complicated structure quite different from that of the stable $\text{Ge}_2\text{Sb}_2\text{Te}_5$ crystalline phase. These strongly suggest that the chemical bonding nature of Se is considerably different from that of Te.

2. EXPERIMENTS

We prepared $\text{Ge}_2\text{Sb}_2(\text{Se}_x\text{Te}_{1-x})_5$ specimens by melting stoichiometric mixtures of 99.999%-pure Ge, Sb, Se, and Te in an argon atmosphere and then quenching it in ice water. The powder specimens produced by crushing the complete ingots were packed in quartz capillary tubes with an internal diameter of 0.3 mm. To insulate them against the atmosphere, we sealed the opening of each capillary with an oxyacetylene flame. We performed diffraction experiments using the BL02B2 beamline at the Japan Synchrotron Radiation Research Institute [3]. The beam energy was about 29.5 keV. Intensity data were collected using a Debye-Scherrer camera with a 287 mm radius. An imaging plate with a pixel area of $100 \mu\text{m}^2$ was used as the detector; by reading the imaging plate for a pixel area of 50mm^2 , intensity data in steps of 0.01° were obtained. The experiments at high temperatures were conducted by blowing N_2 gas at a specified temperature onto the capillary.

For XAFS measurements of Ge, Sb and Se K-edges, BN + $\text{Ge}_2\text{Sb}_2\text{Se}_5$ pellets were prepared adjusting each optimum absorption thickness. These measurements were carried out at the BL14B2 beam line of the Japan Synchrotron Radiation Research Institute (SPring-8) at room temperature. The mean free paths, backscattering amplitudes, and phase shifts were obtained by the FEFF [4] calculations. The Debye temperatures used for the calculations were estimated by performing powder diffraction experiments and the Rietveld analyses using appropriate crystalline specimens.

3. RESULTS & DISCUSSION

Several kinds of $\text{Ge}_2\text{Sb}_2(\text{Se}_x\text{Te}_{1-x})_5$ specimens were measured chiefly by x-ray diffraction methods. Of the results obtained, those of XRD and EXAFS measurements for $\text{Ge}_2\text{Sb}_2\text{Se}_5$ and of XRD measurement for $\text{Ge}_2\text{Sb}_2(\text{Se}_{0.8}\text{Te}_{0.2})_5$ are shown below.

XRD for $\text{Ge}_2\text{Sb}_2\text{Se}_5$

We show the x-ray diffraction patterns of the amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ taken at from RT to about 700 K in Fig. 1, which clearly demonstrates the amorphous phase is stable up to about 560 K ($\sim 290^\circ\text{C}$). Above this temperature or more, Bragg peaks showing the formation of a crystalline phase emerged in the halo pattern of the amorphous phase.

However, the patterns obtained below 546 K are almost the same irrespective of temperature; this strongly suggests that the atomic configuration in this amorphous material remains unchanged hardly depending on temperature. This transition temperature to the crystalline phase is much higher than that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$, about 400 K ($\sim 130^\circ\text{C}$); in addition to this, an intermediate structure like NaCl-type structure was hardly observed via this transformation. $\text{Ge}_2\text{Sb}_2\text{Se}_5$ crystallizes into an orthorhombic structure with very large unit cell size; the atomic configuration is very complicated, which is largely different from that of the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ stable phase (The structure of this crystalline phase is expected to be similar to that of $\text{Pb}_4\text{Sb}_4\text{Se}_{10}$ [5] (Pnma, $24.591 \times 19.757 \times 4.166 \text{ \AA}$); however, the precise structure analysis is being performed). It is known that GeSe [6] (Pnma, $10.83 \times 3.837 \times 4.387 \text{ \AA}$) and Sb_2Se_3 [7] (Pnma, $11.7938 \times 3.9858 \times 11.6478 \text{ \AA}$) have orthorhombic structures as well, and the former can be described as a distorted NaCl-type structure [6]. Through the transformation from the amorphous to the crystalline phase, a simple and isotropic crystalline phase like an NaCl-type structure was hardly observed; however, at the transformation, it is possible that such a transient atomic configuration is locally formed as shown in the following section.

EXAFS for $\alpha\text{-Ge}_2\text{Sb}_2\text{Se}_5$

EXAFS measurements for the amorphous $\text{Ge}_2\text{Sb}_2\text{Se}_5$ were performed at room temperature, which revealed that the coordination structure is very similar to that of the amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [8]. The structural parameters, m , R , B etc. were obtained by least squares curve fitting. The analytical software employed was Rigaku REX2000 [8]. Table I shows a summary of the obtained structural parameters. The coordination numbers obtained do not definitely obey the $8-N$ rule (It is generally believed that in a covalent amorphous state, the IV ($N = 4$) group elements such as Ge, the V ($N = 5$) such as Sb, and the VI ($N = 6$) such as Se have four-, three-, and two-fold coordination, respectively. [9]); however, which approximately shows coincidence with this rule. The deviation in coordination number from the $8-N$ rule has been also found in the amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$ [10]. The pair numbers derived from the obtained coordination numbers satisfy $n_{\text{Ge-Se}} = n_{\text{Se-Ge}}$, $n_{\text{Ge-Sb}} = n_{\text{Sb-Ge}}$, and $n_{\text{Sb-Se}} = n_{\text{Se-Sb}}$ to good extent as shown in Table I, which also demonstrates that the obtained coordination structure was determined in a high precision. From this table, the following preferred coordination, which was also seen in the amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$, can be derived.

- 1) Se-Se pairs are rarely present in this pseudo-binary amorphous compound. In other words, Se is surrounded by only Ge or Sb.
- 2) Ge and Sb bonds more easily to Se than to Ge or to Sb.

This strongly suggests that the $\text{Ge}_2\text{Sb}_2\text{Se}_5$ amorphous compound already contains a large number of atomic networks with the NaCl-type configuration as well as the amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_5$.

XRD for $\text{Ge}_2\text{Sb}_2\text{Se}_{0.8}\text{Te}_{0.2}$

Figure 2 shows the x-ray powder diffraction patterns for $\text{Ge}_2\text{Sb}_2(\text{Se}_{0.8}\text{Te}_{0.2})_5$. This specimen quenched in ice water, without showing an amorphous pattern, was already in a crystalline phase of an NaCl-type structure familiar to us. The structural analysis results for this crystalline phase are shown in Table II and Fig. 3. This NaCl-type crystalline structure was kept up to about 600 K ($\sim 320^\circ\text{C}$); above this temperature or more, peaks of the same orthorhombic structure as has seen in $\text{Ge}_2\text{Sb}_2\text{Se}_5$ notably emerged in the diffraction patterns. This means that Te is very important element for these pseudo-binary compounds to form NaCl-type structures; whereas Se tends to lead the structure to more complicated atomic configuration crystallized in an orthorhombic symmetry. A simple and isotropic structure with six-fold coordination structure like an NaCl-type structure is believed to be one of the indispensable atomic configurations for a phase-change material to enable rapid transformation from an amorphous to a crystalline phase [11]. On the other hand, $\text{Ge}_2\text{Sb}_2\text{Se}_5$ did not show this transient structure through the amorphous-crystal transformation. It is consequently presumed that the fraction of Se or Te in the $\text{GeTe-Sb}_2(\text{Se}_x\text{Te}_{1-x})_3$ compounds strongly affect their phase-change speeds and endurance of the amorphous phases, particularly at Se-rich side.

4. CONCLUSION

The phase transformation from an amorphous phase to a crystalline phase is caused by rearrangement of chemical bonding between both phases via laser irradiation; which strongly suggests that faster crystallization can probably be achieved by raising incident photon density; in other words, by instantaneously supplying sufficiently large heat energy. However, tiny amorphous marks consisting of fewer atoms left on the recording films need to robustly hold their phases for several decades or for several centuries under usual life environment, which asks us for further examination of amorphous stability to realize future ultra-high-density phase-change memories as well. As has shown in this study, it is very likely that the replacement of the atoms in the GST materials by elements with stronger covalent bonding nature provides those materials higher amorphous stabilities.

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Biographyies

Dr. Toshiyuki Matsunaga received his Ph.D. in physics for his work on crystal structures, phase transitions, and bonding natures in intermetallic compounds in 1986 from Hiroshima University in Japan. Since joining Panasonic Corporation (Matsushita Electric Industrial) in 1984, he has developed new electronic devices by analyzing a large number of materials by such surface analysis methods as SEM, XMA, AES, SIMS, and TPD. Since 1996, he has been involved in optical disc R and D, concentrating on basic transition phenomenon research in phase-change recording materials.

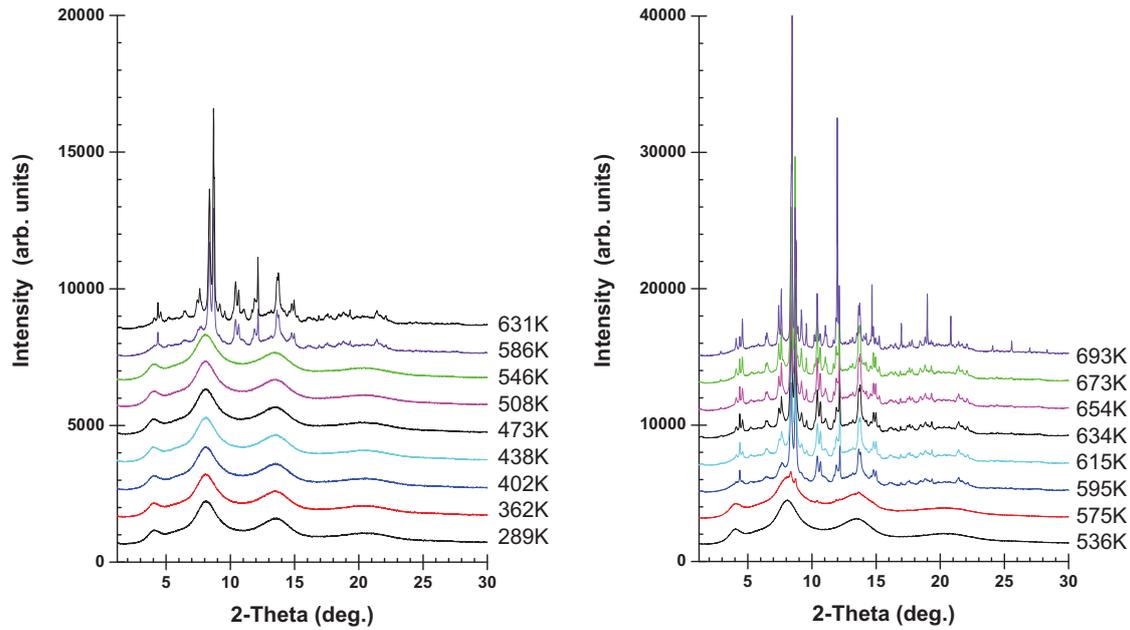


Figure 1. X-ray diffraction patterns for the $\text{Ge}_2\text{Sb}_2\text{Se}_5$ taken at from RT to 693 K (left figure). The measurements were performed twice using two single capillaries.

Table I. Local structure for the amorphous $\text{Ge}_2\text{Sb}_2\text{Se}_5$ determined by EXAFS (RT). The symbols, m , R , and n , represent coordination number, nearest neighbor bond length, and number of atomic pairs respectively, and the suffixes, i and j , indicate the atom species. B indicates Debye-Waller factor (here, $B = 8\pi^2 \langle u^2 \rangle$ where $\langle u^2 \rangle$ is the mean square displacement). The numbers of atomic pairs, which can be obtained by $m_{ij}C_i$, are indicated in terms of a single molecule (C_{Ge} , C_{Sb} , and C_{Se} are 2, 2, and 5, respectively; C_i is proportional to respective atomic concentration.).

atom (i)	pair (i-j)	m_{ij}	R_{ij} (Å)	n_{ij}	B (Å ²)
Ge	Ge-Se	3.7 ± 0.6	2.38 ± 0.01	7.4	0.42 ± 0.01
	Ge-Sb	0.7 ± 0.3	2.67 ± 0.04	1.4	
Sb	Sb-Se	2.4 ± 0.6	2.60 ± 0.01	4.9	0.53 ± 0.04
	Sb-Ge	0.7 ± 0.4	2.68 ± 0.04	1.4	
Se	Sb-Sb	0.5 ± 0.1	2.89 ± 0.01	0.9	0.54 ± 0.05
	Se-Ge	1.5 ± 0.2	2.37 ± 0.02	7.7	
	Se-Sb	0.9 ± 0.4	2.60 ± 0.02	4.5	

Table II. Refined structural parameters for $\text{Ge}_2\text{Sb}_2(\text{Se}_{0.8}\text{Te}_{0.2})_5$ metastable phase at room temperature. Space group is $Fm\bar{3}m$. Standard deviations are shown in parentheses. Final R -factors and lattice parameter are $R_{\text{wp}} = 6.27\%$, $R_p = 3.43\%$, $R_B = 3.13\%$, $R_{\text{wp}} \text{ expected} = 2.66\%$, and $a = 5.7533$ (5) Å.

atom	site	g	x	y	z	$B(\text{Å}^2)$
$\text{Se}_{4/5}\text{Te}_{1/5}$	$4a$	1.0	0	0	0	2.6(2)
$\text{Ge}_{1/2}\text{Sb}_{1/2}$	$4b$	1.01(2)	1/2	1/2	1/2	1.2(1)

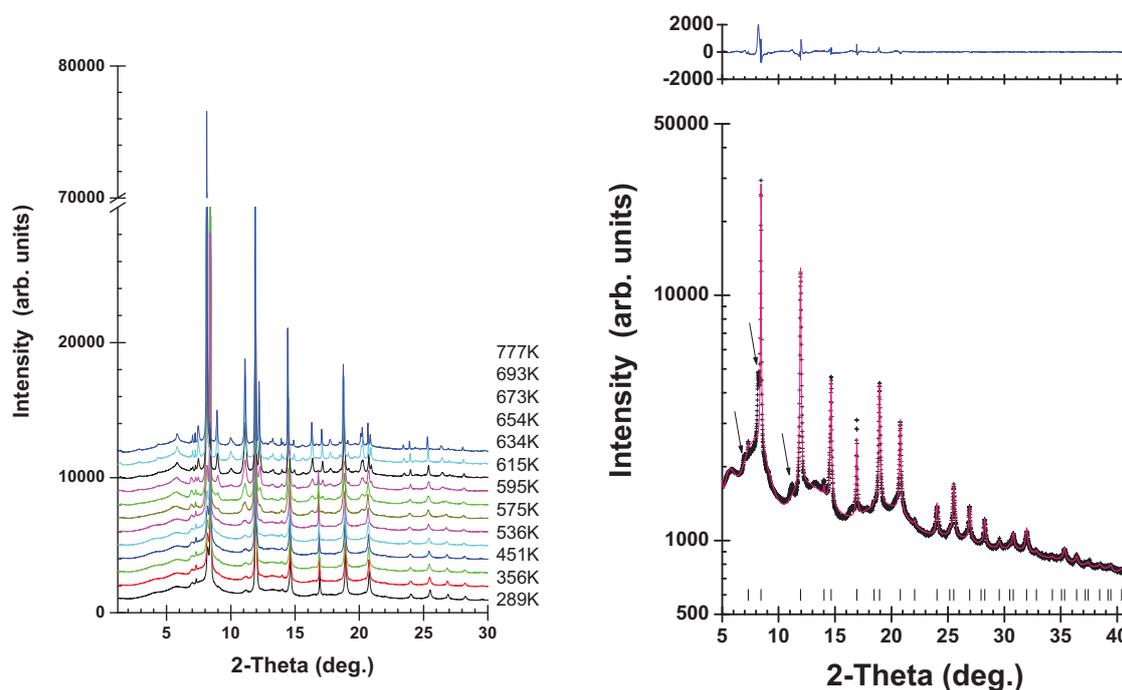


Figure 2 (left figure). X-ray diffraction patterns for the amorphous $\text{Ge}_2\text{Sb}_2(\text{Se}_{0.8}\text{Te}_{0.2})_5$ taken at from RT to 693 K.

Figure 3 (right figure). Observed (+) and calculated (red line) x-ray diffraction profiles of $\text{Ge}_2\text{Sb}_2(\text{Se}_{0.8}\text{Te}_{0.2})_5$ at room temperature obtained by the Rietveld analyses. The program used for these refinements was JANA2000 [12]. A difference curve (observed–calculated) appears at the top of the figure, and under the diffraction patterns, the reflection markers are indicated by vertical spikes. The weak peaks marked by the arrows are those from the stable orthorhombic phase, which means that, although a major part of this powder specimen consists of the NaCl-type crystal, the remaining minor part is already in the stable orthorhombic phase.