Studies of High-Speed Phase-Change Materials Using Synchrotron Radiation

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Abstract

Mechanism of the superior phase-change characteristics was investigated for four kinds of materials: $Te_{60}Ge_4Sn_{11}Au_{25}$, GeTe-$Sb_2Te_3$ system GeTe-Bi_2Te_3 system and $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$, using synchrotron radiations. Based on the results, it was known that i) $GeBi_2Te_4$ film crystallized into simple cubic phase, although $GeSb_2Te_4$ film crystallized into NaCl type structure, ii) $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ film showed a quasi-simple cubic structure at high temperature, and iii) thermal atomic vibration is very large for $Ge_2Sb_2Te_5$ and $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ films as compared with for $Te_{60}Ge_4Sn_{11}Au_{25}$ film. All the facts work to reduce the atomic diffusion length from amorphous to crystalline states, and resultantly shorten the crystallization times of these films. Obtained results also make it possible to explain some outstanding issues; i.g., why the partial substitution of Sb for Bi accelerates the crystallization process of GeTe-Sb_2Te_3system, and why the crystallization rate is controllable by addition of Sb into the pseudo-binaly compositions of GeTe-Sb_2Te_3 system.

I. Introduction

From the end of 1960s to the early 1970s, Ovshinsky's group first demonstrated an epoch-making discovery of laser-induced reversible phase-change phenomenon [1]. Although the compositions of Te-based eutectic alloys did not directly resulted in any optical memory products, a mainstream of R/D in the phase-change optical memory was reconstructed by our proposal of GeTe-Sb_2Te_3 materials in 1987 [2]. The material films resulted in the first commercial product by Matsushita Electric in 1990; and today, several new compositions have been developed and the phase-change memory has become just widely known as optical disk media such as CD-RW, DVD-RW and DVD-RAM. In particular, since 1999, digital video recorders applying rewritable DVDs have been launched as DVD-recorders; they are securely diffusing into our daily lives.

In recent years, we have practiced the structural analyses of these phase-change materials using synchrotron radiations at the Japan Synchrotron Radiation Research Institute (SPring-8) [3],[4]. The main purpose of the study is investigating the mechanism of their superior rapid phase-change process based on the analyses results. About the rapid crystallization mechanism of chalcogenide thin film materials, one of the authors Yamada et al. previously indicated a simple model on TeGeSnAu and GeTe-Sb_2Te_3 systems using Cu-Kα line of conventional x-ray diffract meter and differential scanning calorimetry (DSC). That is, the rapid crystallization speed is due to their crystallization processes not accompanying any phase separation and the highly symmetrical atomic distributions in the produced crystals [5].

Using SPring-8, we tried to obtain more detail structure and temperature dependence of them to discuss more dynamical structural changes. X-ray diffractions using synchrotron radiation beam has

several advantages than using conventional x-ray tube as follows; i.e., i) diffraction patterns with higher resolution can be obtained since highly monochromatic and parallel x-ray is available, ii) precise diffraction data is obtainable with small amount of samples and within a reasonably short time by its intense x-ray, and iii) experiments at high and low temperatures can be carried out promptly.

In this paper, we introduce the analyses results on several materials: TeGeSnAu[6], GeTe-Sb_2Te_3 [7], AgInSbTe [8] and GeTe-Bi_2Te_3 [9], and try to summarize the rapid crystallization mechanism of them. For facilitating the understandings and for concentrating to discussions, details of analyses are boldly omitted, here.

II. Experimental

We investigated the four kinds of phase-change materials: $Te_{60}Ge_4Sn_{11}Au_{25}$, GeTe-$Sb_2Te_3$, GeTe-$Bi_2Te_3$ and $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$. Their characteristics are briefly mentioned below.

1. $Te_{60}Ge_4Sn_{11}Au_{25} = (Te_{0.8}Ge_{0.5}Sn_{0.15})_{75}Au_{25}$

This composition was first reported in 1986. The crystallization time of $Te_{0.8}Ge_{0.5}Sn_{0.15}$ film was remarkably shortened from 30us to 300 ns by addition of Au; at that time, the film crystallized into a meta-stable single phase with infrequent structure of simple cubic structure.

2. GeTe-Sb_2Te_3 pseudo-binary system

It is one of the most popular phase-change materials, and applied for DVD-RAM. It was reported that films on this material system meta-stably crystallized into NaCl type crystal [10]. Here, the non-stoichiometric composition $Ge_6Sb_2Te_9$ [11] was investigated with $GeSb_2Te_4$ and $Ge_2Sb_2Te_5$.

3. $GeBi_2Te_4$

Recently, it was reported that partial substitution of Bi for Sb in GeSbTe was effective to increase crystallization rate [12]. Here, the crystal structure of $GeBi_2Te_4$, one of the stoichiometric compositions in the GeTe-Bi_2Te_3 pseudo-binary system, was representatively examined.

4. $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$

The original report of this thin film was made in 1991[13], and it has been applied for CD-RW and DVD-RW. It is reported that this material has much different characteristics as compared with GeTe-Sb_2Te_3 material system, especially in the crystallization process.

X-ray diffraction data of above-mentioned phase-change materials were collected using synchrotron radiations at BL02B2 beam line of Spring-8. Each material film with a thickness of approximately 500 nm was formed by sputtering on a glass disk 120 mm in diameter. The film was crystallized by means of laser irradiation and then scraped off with a spatula to create a powder. To prepare the experimental specimen for x-ray diffraction, the powder was then packed into a quartz capillary tube with an internal diameter of 0.2 mm. Both ends of the capillary were open to the air. A pre-collimator mirror and a double crystal spectrometer were used to ensure that the incident beam used for the diffraction experiments was highly monochromatic and parallel. The wavelength of the radiation beam was set about 0.42 Å. The camera radius was 278 mm and the pixel area of the imaging plate was 100 μm^2, corresponding to an angular resolution of approximately 0.02°. In order to confirm the radiation beam energy used (29.5keV), the diffraction pattern of powdered CeO_2 (a= 5.4111Å) was taken under the same conditions. The Rietveld method was used to determine the precise structures [14], and RIETAN was used as the analytical program [15]. The experiments of temperature dependence were carried out with spraying the N2 gas to the capillary. The composition of the specimen was determined using inductively coupled plasma atomic emission spectrometry (ICP).

III. Results

Each specimen of laser-crystallized film was poly-crystalline with average grain size of 10 nm. The obtained results of crystal structures and their temperature dependence are described below.

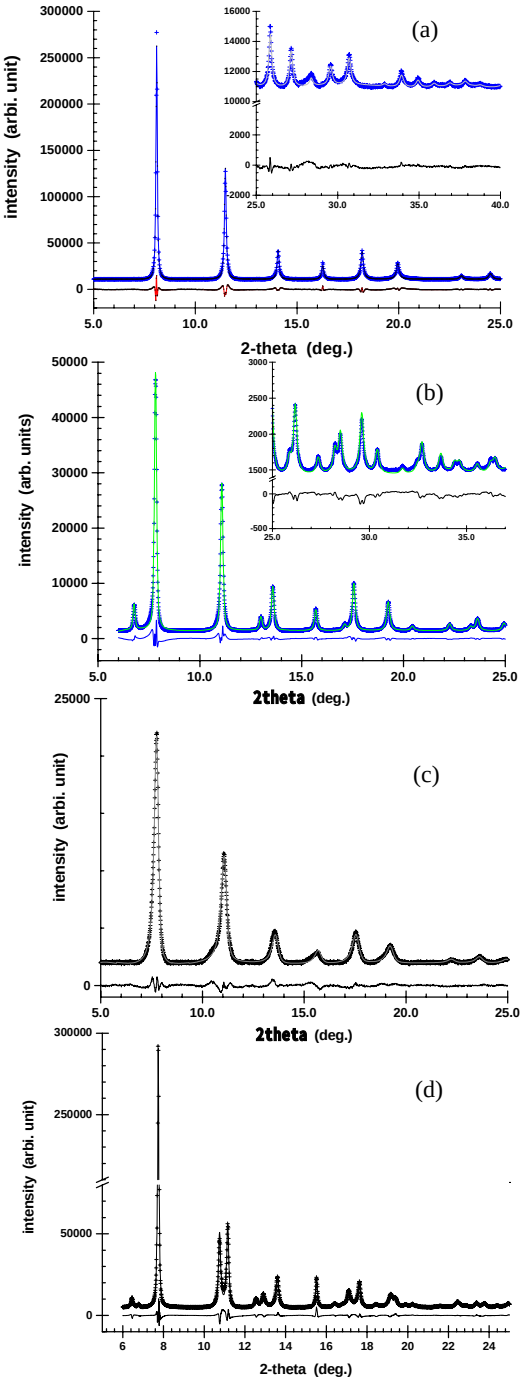

Fig. 1 Observed and calculated diffraction patterns of the powdered specimens: (a)$Te_{60}Ge_4Sn_{11}Au_{25}$, (b)$GeSb_2Te_4$, (c)$GeBi_2Te_4$, and (d)$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$.

1. Diffraction patterns and structure analyses

Figure 1 shows the observed and calculated diffraction patterns of the powdered specimens. It is seen that they show very good agreement in the every case for (a) $Te_{60}Ge_4Sn_{11}Au_{25}$, (b) $GeSb_2Te_4$, (c) $GeBi_2Te_4$, and (d) $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$. We carried out search-match analyses and revealed that each of (a), (b), (c), and (d) is respectively identical to a distinct structure as follows; i.e., (a) is identical to Polonium crystal in the space group of *Pm*-3*m* if temporarily setting the lattice constant to about 3 Å, (b) is identical to LaP, CsF, SrS etc. belonging to the space group of *Fm*-3*m* and having NaCl type structure with a lattice constant a=6.00-6.04 Å, (c) is similar to (a), and (d) is identical to As, Sb, or Bi crystals with A7 structure belonging to the space group of *R*-3*m*. Thus, the assumed crystal structure for each material is shown in Fig.2. The analyses results by the Rietveld method are listed in Table I.

At first, $Te_{60}Ge_4Sn_{11}Au_{25}$ crystal has a simple cubic structure with lattice parameter of about 3 Å, where each component of Te, Ge, Sn, and Au randomly occupies the 1(*a*) site.

Second, both of $GeSb_2Te_4$ and $Ge_6Sb_2Te_9$ crystals have NaCl type structure with lattice parameter of about 6 Å, where Te wholly occupies the 4(*a*) site, and Ge and Sb randomly occupy the 4(*b*) site. There indispensably exist some vacancies in the 4(*b*) site according to the compositions; e.g., 25% and 11% for $GeSb_2Te_4$ and $Ge_6Sb_2Te_9$, respectively. We already reported that the vacancies of $Ge_2Sb_2Te_5$ film is never filled up by addition of excess Sb atoms as a formula of $Ge_2Sb_{2+x}Te_5$ ($0 \leqq x \leqq 1$); the added Sb atoms are probably condensed at the grain boundaries in the amorphous state [7].

Third, it is very interesting that similar compound of $GeBi_2Te_4$ has not NaCl type structure but simple cubic structure with lattice parameter of about 3 Å as same as $Te_{60}Ge_4Sn_{11}Au_{25}$, where each component of Te, Ge, and Bi randomly occupies the 1(*a*) site.

Table I Refined structural parameters and the final *R*-factors and lattice parameters of (a)$Te_{60}Ge_4Sn_{11}Au_{25}$, (b)$Ge_2Sb_2Te_5$ and (d)$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$

Composition	atom	site	*g*	*x*	*y*	*z*	$B(A^2)$	*R*wp	*R*p	*R*I	*R*wp (expected)	*a(A)*
$Te_{80}Ge_4Sn_{11}Au_{25}$	Au,Ge,Sn,Te	1(*a*)	1.0	0	0	0	3.2(5)	2.99%	1.94%	1.02%	0.90%	2.99492(46)
$GeSb_2Te_4$	$Te_{1.0}$	4(*a*)	1.0	0	0	0	1.3(2)	6.08%	4.61%	1.98%	3.52%	6.03686(5)
	$Ge_{0.408}Te_{0.413}$	4(*b*)	1.0	0	0	0	3.6(3)	4.71%	3.24%	1.42%	1.77%	6.00028(26)
$GeSb_2Te_4$	$Te_{1.0}$	4(*a*)	1.0	0	0	0	1.3(2)	6.08%	4.61%	1.98%	3.52%	6.03686(5)
	$Ge_{0.408}Te_{0.413}$	4(*b*)	1.0	0	0	0	3.6(3)	4.71%	3.24%	1.42%	1.77%	6.00028(26)
$GeSb_2Te_4$	$Te_{1.0}$	4(*a*)	1.0	0	0	0	1.3(2)	6.08%	4.61%	1.98%	3.52%	6.03686(5)
	$Ge_{0.408}Te_{0.413}$	4(*b*)	1.0	0	0	0	3.6(3)	4.71%	3.24%	1.42%	1.77%	6.00028(26)
$GeBi_2Te_4$	$Ge_{1/7}Bi_{2/7}Sb_{4/7}$	1(*a*)	1.0	0	0	0	3.7(1)	4.00%	3.01%	1.29%	1.97%	3.0695(7)
$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ (room temp.)	Ag, In, Sb, Te	6(*c*)	1.0	0	0	0.2357(5)	1.52(29)	5.62%	3.96%	0.83%	1.08%	*a*= 4.35530(29) *c*=11.27637(82)
$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ (550C)	Ag, In, Sb, Te	1(*a*)	1.0	0	0	0	5.93(26)	8.22%	6.05%	3.54%	2.55%	*a*= 3.18256(12) *α* =86.835(32)

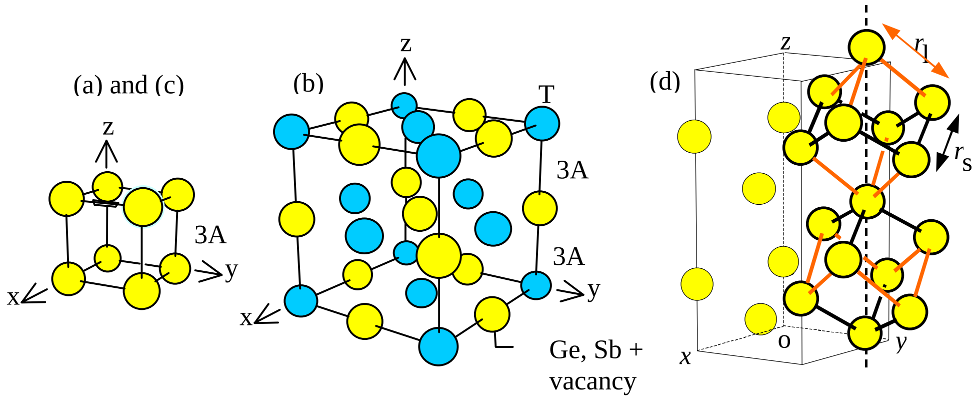

Fig. 2 Identified crystal structure for each specimen: (a)$Te_{60}Ge_4Sn_{11}Au_{25}$,(b)$GeSb_2Te_4$, (c)$GeBi_2Te_4$, and (d) $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$.

At last, $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ crystal has A7 structure belonging to the space group of *R*-3*m* at room temperature; however, as increasing temperature, the relative atomic position gradually changes in the crystal cell, and the crystal is getting to produce the second order phase-transition from A7 to another hexagonal structure that belongs to the space group of *R*32 or *R*3*m* just below melting point. This high temperature phase of rombohedral structure has a lattice constant a=3.182 Å and a bonding angle α=86.8° at 823 K, and the every site is randomly occupied by each component of Ag, In, Sb, and Te. It can be said that the structure has little difference between that of $Te_{60}Ge_4Sn_{11}Au_{25}$ or $GeBi_2Te_4$ with simple cubic structure.

2. Temperature dependence of crystal structures

Figures 3 and 4 show the dependence of lattice parameter *a* and isotropic temperature factor *B* on temperatures, respectively. Based on the results of Fig. 3, the coefficient of linear expansion $\partial L/L\ \partial T$ is calculated for each material, and the coefficient of volume expansion $\partial V/V\ \partial T$ can be estimated to be three times of $\partial L/L\ \partial T$ if assuming an isotropic material. Since the atomic displacement by thermal vibration *u* has a relation of $u^2 = B/8\pi^2$ between the temperature factor of *B*, the increasing rate of the mean square of atomic vibration on temperature *T* can be calculated by $\partial B/B\ \partial T$ based on the results of Fig.4.

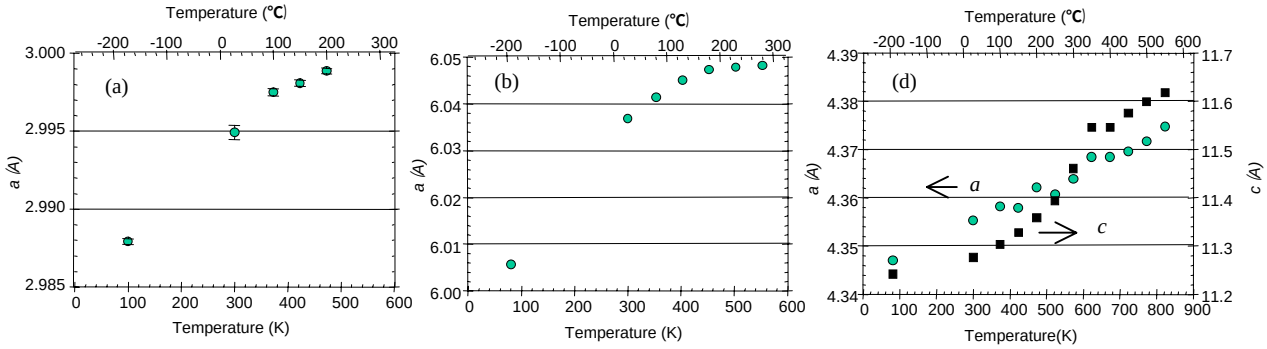

Fig. 3 Temperature dependence of the lattice parameters *a* or c for each specimen: (a) $Te_{60}Ge_4Sn_{11}Au_{25}$, (b) $Ge_2Sb_2Te_5$, and (d) $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$.

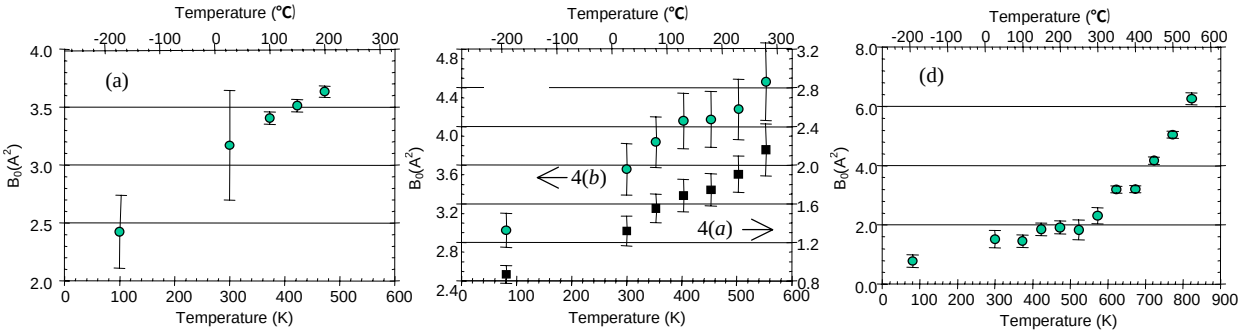

Fig. 4 Temperature dependence of the temperature factors in the Rietveld analyses *B* for each specimen: (a)$Te_{60}Ge_4Sn_{11}Au_{25}$, (b)$Ge_2Sb_2Te_5$, (c)$GeBi_2Te_4$, and (d)$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$.

Table II Observed and calculated diffraction patterns of the powdered specimens: (a)$Te_{60}Ge_4Sn_{11}Au_{25}$, (b)$Ge_2Sb_2Te_5$ and (d)$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$

	$\partial V/V\,\partial T$	$\partial B/B\,\partial T$
$Te_{60}Ge_4Sn_{11}Au_{25}$	3.03×10^{-5}/K	1.05×10^{-3}/K
$Ge_2Sb_2Te_5$	6.24×10^{-5}/K	1.82×10^{-3}/K
$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$	7.09×10^{-5}/K	1.99×10^{-3}/K

The obtained $\partial V/V\,\partial T$ and $\partial B/B\,\partial T$ of the specimens, except for $GeBi_2Te_4$, are listed in Table II. In the first case of $Te_{60}Ge_4Sn_{11}Au_{25}$ (a), it is seen that both of *a* and *B* increase lineally with increased temperature, and $\partial V/V\,\partial T$ was estimated to 3.03×10^{-5}/K, and $\partial B/B\,\partial T$ at room temperature can be calculated to 1.05×10^{-3}/K. In the second case of $Ge_2Sb_2Te_5$ (b), the lattice parameter *a* increases linearly with increased temperature in the low temperature region, however the increasing rate tends to decrease in the high temperature region. $\partial V/V\,\partial T$ at room temperature was about 6.24×10^{-5}/K. On the contrary, the temperature factor *B* shows approximately changes linearly with the temperature for both of 4(*a*) and 4(*b*) sites. It is seen that thermal vibration of the 4(*b*) site, Ge/Sb atoms, is much larger than that of the 4(*a*) site, Te atoms. From the Rietveld analyses, $\partial B/B\,\partial T$ can be calculated to 1.82×10^{-3}/K at room temperature, where equivalent thermal vibration was preconditioned for either of Ge and Sb. In

the last case of $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ (d), the linear expansion in the *c* axis is much larger than in the *a* axis, and $\partial V/V \partial T$ was calculated to be 7.09×10^{-5}/K. The atomic displacement by thermal vibration *B* shows linear increase to temperature at around room temperature; however, it abruptly begins to increase exponentially over around 300K. At just beneath the melting point, the average atomic displacement from the thermal equilibrium position reaches to as high as 10% of the nearest atomic distance of 0.28 Å. The value of $\partial B/B \partial T$ at room temperature is 1.99×10^{-3}/K. The relation between $\partial B/B \partial T$ and $\partial V/V \partial T$ at room temperature is shown for three materials in Fig. 5.

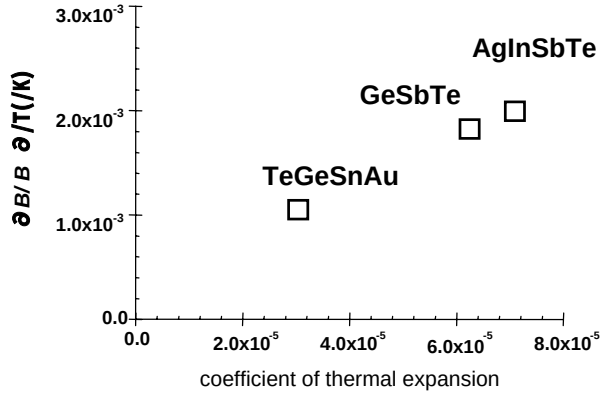

Fig. 5 Relations between the $\partial V/V \partial$ and $\partial B/B$ for specimens of: (a)$Te_{60}Ge_4Sn_{11}Au_{25}$, (b)$Ge_2Sb_2Te_5$, and (d)$Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$

IV. Discussion

We minutely investigated the crystal structures and the thermal properties of four kinds phase-change materials, and found out a few interesting facts relating to their superior phase-change properties. They are summarized as follows:

1) The four kinds materials commonly have highly symmetrical cubic structures, where a any lattice site is randomly occupied by every component element: three of them have simple cubic or quasi-simple cubic structures with a lattice parameter of about 3 Å, and the left one has an NaCl type structure with a lattice parameter of about 6 Å, where the NaCl structure can be regarded as a simple cubic structure with a lattice parameter of about 3 Å if assuming that each element indiscriminately occupies the 4(*a*) and 4(*b*) sites,

2) There exist a strong positive correlation between $\partial V/V \partial T$ and $\partial B/B \partial T$; and $\partial V/V \partial T$ of $Ge_2Sb_2Te_5$ and $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ are much larger than those of the main component elements of Sb and Te, and

3) Considering that the melting point of a solid material is roughly in inverse proportion to its coefficient of thermal expansion, the melting points of 630°C for $Ge_2Sb_2Te_5$ and 550°C for $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ are much higher than the expected values.

From the summary, we can conclude the following mechanism to explain the remarkable phase-change properties of these memory materials. The first is that the rapid crystallization processes are brought about by the crystallization process not accompanying any phase separations and by the highly symmetrical structures of produced crystal phases. This theory is what Yamada et al. have previously reported in 1987, and it was re-confirmed by some recent studies including the present experiments on $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ and $GeBi_2Te_4$ films. Last year, Yusu et al. reported that crystallization process of GeTe-Sb_2Te_3 system was accelerated by partial substitution of Bi for Sb [12]. We suppose the possibility that Bi substitution makes the crystal structure to be simple cubic.

The second is that extremely large thermal atomic vibrations are observed for $Ge_2Sb_2Te_5$ and $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$. In other words, these two materials can be remaining in the crystal state even if the thermal atomic vibrations become very large. We think it means that the atomic distribution in the crystal state becomes further near to that in the amorphous state at high temperature conditions; therefore, the amorphous film easily crystallize only by short atomic diffusions. Here, it is very important that the thermal stability of their amorphous phase is secured since their thermal atomic vibrations are small at room temperature.

From the above discussion, it is considered that the structure difference between the amorphous and crystalline states is rather vague and small for $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$. It means that crystal nucleation is hard to be produced at high temperature. We think this is because the crystal growth from the amorphous mark edge is dominant in the crystallization process of this material. On the contrary, structure difference between in the amorphous and crystalline states is more distinct for $Te_{60}Ge_4Sn_{11}Au_{25}$. Therefore, this material will be crystallized through distinct nucleation and growth process. It is also expected that $Ge_2Sb_2Te_5$ will show the intermediate process between for $Te_{60}Ge_4Sn_{11}Au_{25}$ and $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$.

V. Conclusion

Thorough the analytical study by use of synchrotron radiations, our understandings on crystallization mechanism has made a remarkable progress on the recent phase-change materials. As reported, we have though that the rapid crystallization process is greatly indebted on i) the crystallization process without phase separation and ii) highly symmetrical crystal structure. In this paper, we newly clarified that iii) the large thermal atomic vibration at high temperature conditions also works to shorten the crystallization time by the present study. It is natural to carry out the structural analyses of the amorphous structure in order to make sure our new proposal; we are accordingly planning to examine the atomic distribution in the amorphous phase of these material films. Now it is very interested for us whether the GeTe-Sb_2Te_3 films directly crystallize into the NaCl structure or through the simple cubic phase like $GeBi_2Te_4$. It will be known through the structure study of the amorphous structure. Hereinafter, it will be increasingly important to understand the exact phase-change mechanism for searching advanced materials.

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