

Article



Boundaries of the *X* Phases in Sb–Te and Bi–Te Binary Alloy Systems

Kouichi Kifune ^{1,*}, Takuya Wakiyama ², Hiroki Kanaya ², Yoshiki Kubota ² and Toshiyuki Matsunaga ³

- ¹ Hiroshima Institute of Technology, Faculty of Engineering, 2-1-1 Miyake, Saeki-ku, Hiroshima 731-5193, Japan
- ² Osaka Prefecture University, Graduate School of Science, Osaka 599-8531, Japan
- ³ Department of Materials Science & Engineering, Kyoto University, Kyoto 606-8501, Japan
- * Correspondence: k.kifune.yw@cc.it-hiroshima.ac.jp

Received: 9 August 2019; Accepted: 27 August 2019; Published: 29 August 2019



Abstract: Sb–Te and Bi–Te compounds are key components of thermoelectric or phase change recording devices. These two binary systems form commensurately/incommensurately modulated long-period layer stacking structures known as homologous phases that comprise discrete intermetallic compounds and *X* phases. In the latter, the homologous structures are not discrete but rather appear continuously with varying stacking periods that depend on the binary composition. However, the regions over which these *X* phases exist have not yet been clarified. In this study, precise synchrotron X-ray diffraction analyses of various specimens were conducted. The results demonstrate that the *X* phase regions are located between Sb₂₀Te₃ and Sb₅Te₆ in the Sb–Te system and between Bi₈Te₃ and Bi₄Te₅ in the Bi–Te system.

Keywords: binary alloy; phase diagram; X-ray diffraction; superlattice

1. Introduction

Compounds in the Sb-Te and Bi-Te systems have been widely used as base materials for optical disks and thermoelectric materials, and many studies have attempted to discern their phase diagrams and crystal structures. DVDs and Blu-ray discs, which appeared in the late 1990s, have become ubiquitous recording media in modern society owing to their improved recording densities and fast writing and reading speeds. However, because of the rapidly increasing amount of digital data requiring storage, further improvements in the capacity, reliability, and durability of recording media are desired. The recording films in these media are predominantly composed of GeTe–Sb₂Te₃ (GST) pseudo-binary compounds [1], which are obtained by adding Ge to Sb–Te system (group 15–16) compounds, or Ag–In–Sb–Te (AIST) compounds, which are produced by adding a small amount of Ag and In [2]. Both materials allow the recording or rewriting of data as a result of a reversible transition between crystalline and amorphous phases in response to temperature changes due to irradiation with laser light. The thermoelectric properties of these compounds have been examined so as to improve their performance [3–5], and research has also been performed with Ge–Bi–Te compounds obtained by the addition of Ge [6]. The properties of these materials are highly correlated with their crystal structures; therefore, the improvement of these compounds will require a good understanding of their structures, temperature characteristics and phase changes. Previously, our own group has primarily focused on the crystal structure of Sb–Te-based and Bi–Te-based group 15–16 compounds [7–10].

The structure of group 15–16 chalcogenide compounds consists of atomic layers having a triangular lattice arrangement with a cubic close-packed *ABC* stacking sequence [3,4,11–14]. The structures of Sb–Te compounds contain two different structural blocks: Sb–Sb layers and Te–Sb–Te layers.

These blocks are systematically stacked along the *c*-axis direction. As shown in Figure 1, Sb (having an A7:hR2-type structure) and Sb₂Te₃ (having an hR15-type structure) consist solely of the former and latter blocks, respectively. According to the composition of a particular compound, the number and arrangement of blocks will change, and the general formula may be summarized as $(Sb_2)_n(Sb_2Te_3)_m$ (where *n* and *m* are integers). Compounds with a long-period stacking structure, in which these two basic structures form a eutectic mixture at the unit-cell level, are termed homologous phases [3]. The period of the superlattice of a long-period structure, γ , can be expressed as

$$\gamma = 3(n+3m)/(2n+5m),$$
(1)

where the integer values n and m represent the numbers of each block. The structures of these homologous phases are characterized by the presence of the two types of blocks stacked along the c-axis direction with long periods according to their respective compositions. In the case where the composition is expressed as Sb_{1-y}Te_y (or Bi_{1-y}Te_y), the relationship between the period of the superlattice and the composition is given by

$$y = 2\gamma - 3. \tag{2}$$



Figure 1. Crystal structures of Sb and Sb₂Te₃ projected along the *a*-axis. Yellow spheres represent Sb, and purple spheres represent Te.

In the *X* phase, homologous structures continuously appear in association with specific compositions, and γ can have both rational and irrational number values [10,15]. Because this long-period structure is extremely sensitive to the composition and also varies depending on the heat treatment applied to the specimen, it is important to optimize both the composition and heat treatment. Previously, we analyzed the crystal structures of Sb–Te and Bi–Te chalcogenide compounds with low Te concentrations in detail and confirmed the phase boundaries of the *X* phases [16]. The purpose of the present study was to confirm the regions occupied by the *X* phases and the Te-rich phase boundaries in both systems.

2. Materials and Methods

Ten specimens in the Sb–Te system were prepared, with Te concentrations in the range of 43.0 to 60.0 at%. These were synthesized by transferring the appropriate quantities of Sb and Te grains into

3 of 10

quartz tubes filled with Ar. These tubes were subsequently sealed then heated in an electric furnace (Shibao Co. Ltd., Osaka, Japan) at 1173 K for 30 min to melt the raw ingredients. After quenching in ice water, the tubes were subjected to a prolonged heat treatment at 773 K for 88 days. In the case of the Bi–Te system, seven specimens with Te concentrations ranging from 53.3 to 59.0 at% were prepared. After heating, melting, and quenching in the same manner as for the Sb–Te system, heat treatment was applied at 723 K for 48 days. In preparation for X-ray diffraction (XRD) analyses, the specimens were ground in a mortar and passed through a 440 mesh (32 μ m) sieve to obtain a uniform microparticle size. The powder specimens were transferred into quartz capillary tubes (each having an internal diameter of 0.3 mm for the Sb–Te-system specimens and 0.2 mm for the Bi–Te-system specimens), after which the tubes were evacuated and sealed under Ar gas.

XRD data were acquired using the SPring-8 powder diffraction BL02B2 beam line. The experimental apparatus included a large Debye–Scherrer camera acting as a transmission-type powder diffractometer and an imaging plate as the detector, as well as the application of high-energy X-rays with a wavelength of 0.042 nm and acquisition of the diffraction pattern at diffraction angles (20) from 0° to 80°. When examining the Sb–Te system, patterns were obtained at 90 K by blowing nitrogen gas over the capillary, while data for the Bi–Te system were acquired at room temperature [17]. XRD data were analyzed by the four-dimensional Le Bail method based on the pattern decomposition of the diffraction profile [18]. The basic unit cell consisted of three cubic close-packed *ABC* layers, and the superspace group was $R-3m(00\gamma)$, refining the lattice constants, profile functions, and background functions via the least-squares method using the JANA2006 software package [19].

3. Results and Discussion

3.1. Sb-Te System

Figure 2 shows the powder XRD profiles for the ten Sb–Te-system specimens. Relatively intense peaks corresponding to pure Sb having an A7-type structure ($\gamma = 3/2$) are evident in each case. As noted in Section 1, A7-type is the basic homologous structure in this system. The less intense peaks at approximately 2.2° and 4.9° are superlattice diffraction lines that are characteristic of the long-period stacked structure of the specimens. Because the peak positions were shifted depending on the specimen, it is evident that a suitable heat treatment (see Materials and Methods section) imparted superlattice periods to the homologous structures that varied depending on the composition.



Figure 2. X-ray powder diffraction profiles of Sb-Te specimens acquired at 90 K.

Figure 3 presents the diffraction profiles of five of these specimens, magnified over the range of $4^{\circ}-8^{\circ}$. The samples with compositions from $Sb_{57}Te_{43}$ to $Sb_{48}Te_{52}$ and the $Sb_{40}Te_{60}$ specimen can be regarded as having crystallized into their respective single structures, whereas the $Sb_{45}Te_{55}$ sample was composed of two coexisting phases. These profiles were analyzed using the Le Bail method, and the resulting lattice constants, superlattice periods, and reliability factors are provided in Table 1. The two phases present in the $Sb_{45}Te_{55}$ specimen were identified as Sb_5Te_6 and Sb_2Te_3 based on calculating the atomic compositions using Equation (2). The *a*-axis length hardly changes as the Te concentration increases, while the *c*-axis value increases gradually up to 54.5 at% Te. The coexistence of two phases does not appear at Te concentrations below that in Sb_5Te_6 (54.5 at% Te), as can be seen from the diffraction patterns of the $Sb_{57}Te_{43}$, $Sb_{51}Te_{49}$, and $Sb_{48}Te_{52}$. These results demonstrate that an X phase definitely exists in the Sb-Te binary system and that Sb_5Te_6 represents the Te side boundary of the X phase on the Te-rich side.



Figure 3. X-ray powder diffraction profiles of Sb–Te specimens acquired at 90 K. The horizontal axis has been enlarged and the intensities are plotted on a logarithmic scale to emphasize the weaker peaks. The arrows indicate peak splitting due to phase separation: A and B correspond to reflections from the Sb₂Te₃ and Sb₅Te₆ phases, respectively.

Table 1. Refined lattice parameters and final *R* factors for Sb–Te. The diffraction data used for the analysis were acquired over the 2θ range of 1.8° to 50.0° .

Specimen	Sb ₅₇ Te ₄₃	Sb ₅₁ Te ₄₉	Sb ₄₈ Te ₅₂ Sb ₄₅ Te ₅₅		Te ₅₅	Sb ₄₀ Te ₆₀	
at.% Te (prepared)	43.0	49.0	52.0	55.0		60.0	
a [nm]	0.425620(6)	0.426641(5)	0.425619(4)	0.425002(8)	0.425034(6)	0.426206(5)	
<i>c</i> [nm]	0.59664(2)	0.598108(12)	0.599744(11)	0.60097(2)	0.60286(2)	0.606914(10)	
γ	1.7344(3)	1.75182(13)	1.76630(9)	1.7728(2)	1.7991(3)	1.80000(6)	
at.%Te (calculated)	46.9	50.4	53.3	54.5	59.8	60.0	
Phase	Sb ₁₇ Te ₁₅	SbTe	Sb ₇ Te ₈	Sb ₅ Te ₆	Sb ₂ Te ₃	Sb ₂ Te ₃	
Phase fraction [%]	100	100	100	50.2(2)	49.8(2)	100	
R _p [%]	3.19	4.29	5.69	5.3	37	4.64	
R _{wp} [%]	4.95	6.91	9.03	8.98		7.70	

Based on our previous study [16], the boundary of the X phase on the Sb-rich side is the $Sb_{20}Te_3$ compound, with a Te concentration of 13.0 at%. In combination with the results obtained in the present

study, it is apparent that the X phase region in the Sb–Te binary system is widely distributed through compositions ranging from 13.0 to 54.5 at% Te (Figure 4).



Figure 4. The *X* phase composition region in the Sb–Te binary system.

3.2. Bi-Te System

Figure 5 presents the powder XRD profiles of seven Bi–Te-system specimens. As was also observed with the Sb–Te system, intense peaks attributed to the fundamental *A*7-type structure are present. In addition, the less intense peaks in the 2θ range of 2.2° – 4.9° are characteristic of the superlattice structure of each specimen. The peak positions were shifted along with the Te concentration, strongly suggesting that these homologous structures have different superlattice periods that vary with composition. These same diffraction patterns magnified in the vicinity of 2.2° for each specimen are shown in Figure 6. Here, it can be seen that two phases were present in both the Bi₄₃Te₅₇ and Bi₄₁Te₅₉ specimens, whereas the other specimens consisted of a single phase.



Figure 5. X-ray powder diffraction profiles of Bi–Te specimens acquired at 300 K.



Figure 6. X-ray powder diffraction profiles of Bi–Te specimens acquired at 300 K. The horizontal axis has been enlarged, and the vertical axis is plotted with a logarithmic scale to emphasize the weaker peaks. The arrows indicate peak splitting due to phase separation: A, B, C, and D correspond to reflections from the Bi₄Te₅, Bi₃Te₄, Bi₁₃Te₁₈, and Bi₂Te₃ phases, respectively.

The results obtained by analyzing these XRD profiles by the Le Bail method are summarized in Table 2, which includes the atomic compositions of the specimens as calculated from the γ values by Equation (2). These data confirm that the Bi₄₇Te₅₃, Bi₄₆Te₅₄, Bi₄₅Te₅₅, and Bi₄₄Te₅₆ were all single-phase compounds and thus were all in the *X* phase. In contrast, the Bi₄₃Te₅₇ specimen consisted of Bi₄Te₅ and Bi₃Te₄ phases. This result shows that the boundary of the *X* phase on the Te-rich side is Bi₄Te₅. The Bi₄₂Te₅₈ coincidentally crystallized into a single Bi₃Te₄ phase, while the Bi₄₁Te₅₉ specimen was composed of Bi₁₃Te₁₈ and Bi₂Te₃, showing that the Bi₁₃Te₁₈ phase exists between Bi₃Te₄ and Bi₂Te₃. It is very interesting that, in contrast to the Bi–Te system, there are no intermetallic compounds between Sb₅Te₆ and Sb₂Te₃ in the Sb–Te system (Figure 4). In our prior work [16], we found that the boundary of the *X* phase on the Bi-rich side is a Bi₈Te₃ compound with 27.3 at% Te. Considering this previous result together with the data obtained in the present study, it can be concluded that the *X* phase region is distributed from 27.3 to 55.7 at% Te (Figure 7). Furthermore, the two phases Bi₃Te₄ and Bi₁₃Te₁₈ appear in the region between the *X* phase and the Bi₂Te₃ phase.

Specimen	Bi ₄₇ Te ₅₃	Bi ₄₆ Te ₅₄	Bi45Te55	Bi ₄₄ Te ₅₆	Bi ₄₃ 7	Г е ₅₇	Bi ₄₂ Te ₅₈	Bi ₄₁	Te ₅₉
at.% Te (prepared)	53.3	54.6	55.6	56.3	57.1		58.1	59.0	
<i>a</i> [nm]	0.441585(11)	0.440950(6)	0.440745(5)	0.440142(10)	0.439738(7)	0.43895	0.43895(2)	0.438489(6)	0.437404(10)
<i>c</i> [nm]	0.59892(2)	0.599164(12)	0.59986(2)	0.60034(2)	0.60080(2)	0.60352	0.60352(3)	0.605068(13)	0.60829(2)
γ	1.76013(12)	1.76572(12)	1.7703(2)	1.77351(11)	1.7783(2)	1.7859	1.7859(2)	1.79038(13)	1.8
at.% Te(calculated)	52.0	53.1	54.1	54.7	55.7	57.2	57.2	58.1	60.0
Phase	Bi ₁₂ Te ₁₃	Bi15Te17	$Bi_{11}Te_{13}$	Bi ₁₉ Te ₂₃	Bi ₄ Te ₅	Bi ₃ Te ₄	Bi ₃ Te ₄	Bi ₁₃ Te ₁₈	Bi ₂ Te ₃
Phase fraction [%]	100	100	100	100	61.2(2)	38.8(2)	100	45.6(2)	54.4(2)
R _p [%]	2.41	2.81	3.22	3.18	2.24		5.19	2.32	
R_{wp} [%]	4.07	4.87	5.35	5.3	3.94		8.57	3.91	

Table 2. Refined lattice parameters and final *R* factors for Bi–Te. The diffraction data used for the analysis were acquired in the 2θ range of 1.8° to 50.0°.

Bi





Figure 7. The *X* phase composition region in the Bi–Te binary system.

Figure 8 plots the lattice constants of the fundamental cell for each phase obtained in this work as a function of the calculated Te concentration in the Bi–Te binary system. The *a*-axis length decreases linearly as the Te concentration increases, while the *c*-axis value increases gradually up to 55.7 at% Te, after which it increases more rapidly, going from 55.7 to 60 at% Te. This change at 55.7 at% Te corresponds to the *X* phase boundary associated with Bi_4Te_5 . Bos et al. also evaluated the crystal structure and physical properties of the Bi–Te system and determined that these properties change abruptly at 53 at% Te [4]. The structure of the Bi_4Te_5 phase is expressed (Bi_2)₁(Bi_2Te_3)₅. These results suggest that the characteristic structure of the Bi_2Te_3 phase (that is, Te–Te layers between Te–Bi–Te–Bi–Te layers) becomes dominant at this boundary, leading to a change in the structure.



Figure 8. The fundamental lattice constants *a* (diamonds) and *c* (circles) as functions of the Te concentration in the Bi–Te binary system.

4. Conclusions

In this study, XRD was used to analyze Sb–Te and Bi–Te binary system specimens having high Te concentrations. It was determined that X phase regions were present among the characteristic

homologous phases of these systems, and that the stacking periods of these *X* phases continuously changed along with the specimen composition. In the Sb–Te system, this region occurred in samples with compositions ranging from $Sb_{20}Te_3$ (13.0 at% Te) to Sb_5Te_6 (54.5 at% Te), whereas in the Bi–Te system, this was observed in specimens with compositions ranging from Bi_8Te_3 (27.3 at% Te) to Bi_4Te_5 (55.7 at% Te).

Author Contributions: K.K., Y.K., and T.M. conceived and designed the experiments. K.K., T.W., H.K., Y.K., and T.M. performed the experiments, analyzed the data, and wrote the paper.

Funding: This research received no external funding.

Acknowledgments: The synchrotron radiation experiments were performed on the BL02B2 beamline at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal Nos. 2013A1707, 2013B0084, 2014A1367, 2014B1404, 2015A0074, 2015B0074, 2016A0074, 2016A1370, 2016B0074 and 2017A1272). The authors wish to express their sincere gratitude to S. Kawaguchi and J. Kim at JASRI.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Wuttig, M.; Yamada, N. Phase-change materials for rewriteable data storage. *Nat. Mater.* **2007**, *6*, 824–832. [CrossRef] [PubMed]
- Matsunaga, T.; Akola, J.; Kohara, S.; Honma, T.; Kobayashi, K.; Ikenaga, E.; Jones, R.O.; Yamada, N.; Takata, M.; Kojima, R. From local structure to nanosecond recrystallization dynamics in AgInSbTe phase-change materials. *Nat. Mater.* 2011, *10*, 129–134. [CrossRef] [PubMed]
- Poudeu, P.F.P.; Kanatzidis, M.G. Design in solid state chemistry based on phase homologies. Sb₄Te₃ and Sb₈Te₉ as new members of the series (Sb₂Te₃)_m·(Sb₂)_n. *Chem. Commun.* 2005, 21, 2672–2674. [CrossRef] [PubMed]
- 4. Bos, J.W.G.; Zandbergen, H.W.; Lee, M.H.; Ong, N.P.; Cava, R.J. Structures and thermoelectric properties of the infinitely adaptive series (Bi₂)_{*m*}(Bi₂Te₃)_{*n*}. *Phys. Rev.* **2007**, *B75*, 195203. [CrossRef]
- Kosuga, A.; Nakaia, K.; Matsuzawa, M.; Fujii, Y.; Funahashi, R.; Tachizawa, T.; Kubota, Y.; Kifune, K. Crystal structure, microstructure, and thermoelectric properties of GeSb₆Te₁₀ prepared by spark plasma sintering. *J. Alloy. Comp.* 2015, *618*, 463–468. [CrossRef]
- Omoto, T.; Kanaya, H.; Ishibashi, H.; Kubota, Y.; Kifune, K.; Kosuga, A. Formation phases and electrical properties of Ge-Bi-Te compounds with homologous structures. *J. Electron. Mater.* 2015, 45, 1478–1483. [CrossRef]
- 7. Kifune, K.; Kubota, Y.; Matsunaga, T.; Yamada, N. Extremely long period-stacking structure in the Sb-Te binary system. *Acta Cryst.* **2005**, *B61*, 492–497. [CrossRef] [PubMed]
- 8. Kifune, K.; Fujita, T.; Kubota, Y.; Yamada, N.; Matsunaga, T. Crystallization of the chalcogenide compound Sb₈Te₃. *Acta Cryst.* **2011**, *B67*, 381–385. [CrossRef] [PubMed]
- 9. Matsunaga, T.; Kojima, R.; Yamada, N.; Kubota, Y.; Kifune, K. Structural transformation of Sb-based high-speed phase-change material. *Acta Cryst.* **2012**, *B68*, 559–570. [CrossRef] [PubMed]
- 10. Kifune, K.; Fujita, T.; Tachizawa, T.; Kubota, Y.; Yamada, N.; Matsunaga, T. Crystal structures of X-phase in the Sb-Te binary alloy system. *Cryst. Res. Technol.* **2013**, *48*, 1011–1021. [CrossRef]
- 11. Ghosh, G. The Sb-Te (antimony-tellurium) system. J. Phase Equilibria 1994, 15, 349–360. [CrossRef]
- 12. Okamoto, H. The Bi-Se (bismuth-selenium) system. J. Phase Equilibria 1994, 15, 195–201. [CrossRef]
- 13. Shelimova, L.E.; Karpinsky, O.G.; Zemskov, V.S.; Konstantinov, P.P. Structural and electrical properties of layered tetradymite-like compounds in the GeTe-Bi₂Te₃ and GeTe-Sb₂Te₃ systems. *Inorg. Mater.* **2000**, *36*, 235–242. [CrossRef]
- Lind, H.; Lidin, S. A general structure model for Bi-Se phases using a superspace formalism. *Solid State Sci.* 2003, *5*, 47–57. [CrossRef]
- 15. Kim, W.S.; Chao, G.Y. Phase relations in the system Pt-Sb-Te. Canadian Mineral. 1990, 28, 675-685.
- 16. Kifune, K.; Tachizawa, T.; Kanaya, H.; Kubota, Y.; Yamada, N.; Matsunaga, T. Boundaries of the homologous phases in Sb-Te and Bi-Te binary alloy systems. *J. Alloy. Comp.* **2015**, *645*, 382–387. [CrossRef]

- Nishibori, E.; Takata, M.; Kato, K.; Sakata, M.; Kubota, Y.; Aoyagi, S.; Kuroiwa, Y.; Yamakata, M.; Ikeda, N. The large Debye-Scherrer camera installed at SPring-8 BL02B2 for charge density studies. *Nucl. Instrum. Methods Phys. Res.* 2001, *A467–A468*, 1045–1048. [CrossRef]
- 18. Le Bail, A.; Duroy, H.; Fourquet, J.L. Ab-initio structure determination of LiSbWO₆ by X-ray powder diffraction. *Mater. Res. Bull.* **1988**, 23, 447–452. [CrossRef]
- Petříček, V.; Dušek, M. *The Crystallographic Computing System*; Institute of Physics, Academy of Sciences of the Czech Republic: Praha, Czech Republic, 2006; Available online: http://www.usc.es/export9/ sites/webinstitucional/gl/investigacion/riaidt/raiosx/descargas/manuais/manual_jana98.pdf. (accessed on 27 August 2019).



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).