Inorg. Chem. **2006**, *45*, 2235–2241

Inorganic Chemistry
Article

Single Structure Widely Distributed in a GeTe–Sb_2Te_3 Pseudobinary System: A Rock Salt Structure is Retained by Intrinsically Containing an Enormous Number of Vacancies within its Crystal

Toshiyuki Matsunaga,*,†,§ Rie Kojima,‡ Noboru Yamada,‡,§ Kouichi Kifune,∥ Yoshiki Kubota,⊥ Yoshikazu Tabata,# and Masaki Takata§,£

Characterization Technology Group, Matsushita Technoresearch, Inc., 3-1-1 Yagumo-Nakamachi, Moriguchi, Osaka 570-8501, Japan, AV Core Technology Development Center, Matsushita Electric Industrial Co., Ltd., Osaka, Japan, CREST-JST, Faculty of Liberal Arts and Sciences, Osaka Prefecture University, Osaka, Japan, Graduate School of Science, Osaka Prefecture University, Osaka, Japan, Graduate School of Science, Osaka University, Osaka, Japan, and Japan Synchrotron Radiation Research Institute, Hyogo, Japan

Received September 29, 2005

GeTe(1–x)–Sb_2Te_3(x) sputtered amorphous film was crystallized into a simple NaCl-type structure through instantaneous laser irradiation over a wide composition range from $x = 0$ to at least 2/3. When the ratio of Sb_2Te_3 increases, a vacancy is generated at every Na site for two Sb atoms. The fraction of vacancies, $v(x)$, changes according to $x/(1 + 2x)$, and the cubic root unit cell volume varies with a strong correlation to $v(x)$. Through these created vacancies, valence electrons provided by adjacent Ge/Sb and Te atoms remain constant regardless of the composition, ensuring that these electrons occupy predominantly the bonding molecular orbitals. This results in crystal chemical stability, with the closed shell p–p bondings in the valence electrons arranging the crystal's atomic configuration into an NaCl-type structure.

Introduction

On a rewritable laser disk such as a DVD-RAM (digital versatile disc-random access memory), information is recorded using changes in optical characteristics such as reflectivity and transmissivity caused by the phase change of the material. The most commonly used recording material today is GeTe−Sb_2Te_3 pseudobinary compound. A recording film made of this material can be switched rapidly and reversibly between the crystalline phase, which has a metastable NaCl-type structure,[1] and the amorphous phase under brief irradiation (several tens of nanoseconds) by a laser beam.[2] For many years, it has been known that this pseudobinary compound forms three intermetallic compounds with fairly complicated structures ($Ge_2Sb_2Te_5$, $GeSb_2Te_4$, and $GeSb_4Te_7$) in a thermally equilibrated state.[3] These three compounds can be described as structures with cubic close-packed periodicity, in which the stacking rules of the Ge, Sb, and Te layers are different from each other. The stacking periods of $Ge_2Sb_2Te_5$, $GeSb_2Te_4$, and $GeSb_4Te_7$ comprise 9, 21, and 12 layers, respectively.[4,5] Some other intermetallic compounds, $Ge_3Sb_2Te_6$ (33-layer), $Ge_4Sb_2Te_7$ (39-layer), $GeSb_6Te_{10}$ (51-layer), and $GeSb_8Te_{13}$ (66-layer), have recently been found for this system.[6] The compounds of both ends of the system, GeTe and Sb_2Te_3, are described respectively as 6- (NaCl-type) and 15-layer structures.[7,8]

---

* To whom correspondence should be addressed. Phone: +81-6-6906-4916. Fax: +81-6-6906-3407. E-mail: matsunaga.toshiyuki@jp.panasonic.com.

† Characterization Technology Group, Matsushita Technoresearch, Inc.

‡ AV Core Technology Development Centre, Matsushita Electric Industrial Co., Ltd.

§ CREST-JST.

∥ Faculty of Liberal Arts and Sciences, Osaka Prefecture University.

⊥ Graduate School of Science, Osaka Prefecture University.

\# Graduate School of Science, Osaka University.

£ Japan Synchrotron Radiation Research Institute.

(1) Yamada, N. *MRS Bull.* **1996**, *21* (9), 48.

(2) Yamada, N.; Ohno, E.; Nishiuchi, K.; Akahira, N.; Takao, M. *J. Appl. Phys.* **1991**, *69* (5), 1, 2849.

(3) Abrikosov, N. Kh.; Danilova-Dobryakova, G. T. *Izv. Akad. Auk. SSSR Neorg. Mater.* **1965**, *1*, 204.

(4) Petrov, I. I.; Imamov, R. M.; Pinsker, Z. G. *Sov. Phys. Crystallogr.* **1968**, *13*, 339.

(5) Agaev, K. A.; Talybov, A. G. *Sov. Phys. Crystallogr.* **1966**, *11*, 400.

(6) Shelimova, L. E.; Karpinsky, O. G.; Konstantinov, P. P.; Kretova, M. A.; Avilon, E. S.; Zemskov, V. S. *Inorg. Mater.* **2001**, *37*, 4, 342.

(7) Goldak, J.; Barrett, C. S.; Innes, D.; Youdelis, W. *J. Chem. Phys.* **1966**, *44*, 3323.

(8) Anderson, T. L.; Krause, H. B. *Acta Crystallogr. B* **1974**, *30*, 1307.

10.1021/ic051677w CCC: $33.50

However, the GeTe(1−x)−Sb_2Te_3(x) pseudobinary compound film maintains the same NaCl-type structure as GeTe over a wide range of compositions from $x = 0$ to at least 2/3 when subjected to instantaneous heating by laser irradiation followed by equally rapid cooling. We conducted precise electronic structure analyses and crystal structure analyses of more than a dozen of these laser-crystallized specimens of varying compositions and investigated their structural characteristics to gain an understanding of why, in this pseudobinary system, the NaCl-type structure continuously appears over such a wide composition range.

Experimental Section

Sample Preparation. The specimens for diffraction measurement were made using the following method. First, GeTe−Sb_2Te_3 thin films with a thickness of about 3000 Å were deposited onto glass disks with a diameter of 120 mm by DC magnetron sputtering from compound targets in an Ar gas atmosphere. The compositions of the films were examined using inductively coupled plasma atomic emission spectrometry (ICP). The films were amorphous just after their formation and were crystallized by laser irradiation into cubic or rhombohedral NaCl-type structures. Each film was then powdered by being scraped with a spatula. The powder was packed into a quartz capillary tube with an inner diameter of 0.2 mm for use in the diffraction experiments using synchrotron radiation. The opening of the capillary was sealed by melting with an oxyacetylene flame to insulate the sample against the atmosphere.

X-ray Diffraction Analysis. The diffraction experiments were performed using the BL02B2 beam line at the Japan Synchrotron Radiation Research Institute (SPring-8).[9] A precollimator mirror and a double-crystal monochromator were used to ensure that the incident beam used for the diffraction experiments was highly monochromatic and parallel. The energy of the incident beam was about 29.5 keV. Diffraction intensities were measured using a Debye−Scherrer camera with a radius of 287 mm. An imaging plate with a pixel area of 100 μm^2 was used as the detector. Angular resolution was 0.02°. The crystal structures were refined using the Rietveld method.[10] The program used was RIETAN.[11] To improve the accuracy of the Rietveld analysis, intensity data in steps of 0.01° were obtained by reading the imaging plate for a pixel area of 50 μm^2. The energies of the synchrotron radiation used were confirmed by recording the diffraction intensity of CeO_2 ($a = 5.4111$ Å) powder as a reference specimen at room temperature under the same conditions. Neutral atomic scattering factors were used for the structural analyses, and isotropic thermal vibrations were assumed for each atomic site.

Results and Discussion

Overview of the Crystal Structures. Diffraction investigations were conducted on 17 specimens: GeTe/Sb_2Te_3 = 1:0, 22:1, 13:1, 21:2, 10:1, 8:1, 6:1, 9:2, 4:1, 7:2, 3:1, 5:2, 2:1 (3 items), 1:1, and 1:2. At room temperature, the first six specimens crystallized into a rhombohedral phase with a slightly deformed NaCl-type structure, and the rest crystallized into an NaCl-type cubic phase. We have previously reported the structural analysis results for these NaCl-type cubic crystals in several papers.[12,13] This structure belongs to the $Fm\bar{3}m$ space group. Te occupies 100% of 4(a) sites, while Ge, Sb, and vacancies are randomly located at 4(b) sites. On the other hand, the six specimens on the GeTe-rich side have a rhombohedral structure with an NaCl-type atomic arrangement, which can be described as a cubic NaCl-type structure that has been slightly deformed along one of the 3-fold rotation axes (Figure 1). Figure 2 and Table 1 show the results of the structural analysis of $Ge_{10}Sb_2Te_{13}$ (10:1). The structure is an isostructure of the GeTe low-temperature rhombohedral phase. As seen in Table 1, although the rhombohedral angle narrows slightly from 60° in the cubic phase, and Ge/Sb + vacancy and Te generate a small mutual shift from their equilibrium positions in the cubic phase, the structure can basically be regarded as being of the NaCl type. $Ge_{10}Sb_2Te_{13}$ exhibits a structural transformation to the NaCl-type cubic phase at about 430 K. GeTe (1:0) transforms to the cubic phase at around 700 K.[14]

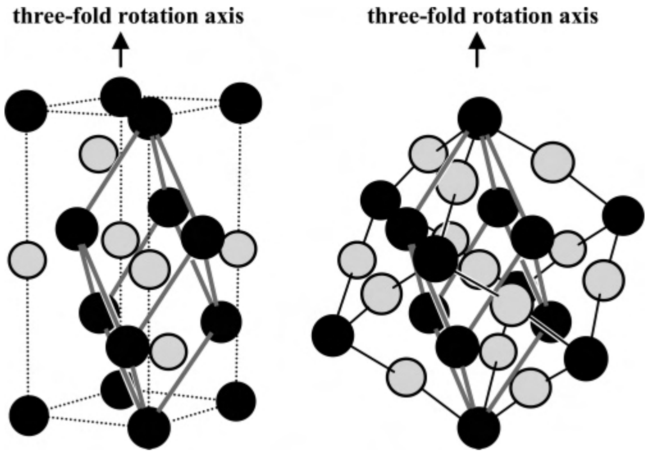


Figure 1. Structure of the distorted NaCl-type low-temperature phase shown with both the rhombohedral (gray thick lines) and hexagonal (dotted lines) unit cells (left). Black circles indicate Te atoms, whereas gray ones represent Ge/Sb atoms and vacancies. The NaCl-type cubic structure of the high-temperature phase, framed by thin solid lines, is slightly deformed in the low-temperature phase (right).

Crystallographic and Bonding Natures of GeTe. We performed band and molecular orbital calculations to examine the electronic structures in GeTe. The lattice constants and Ge atomic position used for both calculations were $a = 4.2708(5)$ Å, $\alpha = 58.459(6)°$, and $x = 0.5300(2)$ at room temperature. (The figures in parentheses represent standard deviations. The interatomic distances obtained are tabulated in Table 2.) These parameters are our Rietveld analysis result (cf. Table 1). The program used for the band calculation based on the density functional theory is CHASE-3PT (PHASE).[15] The calculations were performed using the generalized gradient approximation in the plane-wave method. The density of state (DOS) obtained, which is shown in

---

[9] Nishibori, E.; Takata, M.; Kato, K.; Sakata, M.; Kubota, Y.; Aoyagi, S.; Kuroiwa, Y.; Yamakata, M.; Ikeda, N. *Nucl. Instrum. Methods* **2001**, *A467−468*, 1045.

[10] Rietveld, H. M. *J. Appl. Cryst*. **1969**, *2*, 65.

[11] Izumi, F.; Ikeda, T. *Mater. Sci. Forum* **2000**, *321−324*, 198.

[12] Matsunaga, T.; Yamada, N. *Phys. Rev. B* **2004**, *69*, 10, 104111.

[13] Matsunaga, T.; Yamada, N.; Kubota, Y. *Acta Crystallogr. B* **2004**, *60*, 685.

[14] Bierly, J. N.; Muldawer, L.; Beckman, O. *Acta Metall*. **1963**, *11*, 447.

[15] The "PHASE" computer program was created by the members of the national project "Frontier Simulation Software for Industrial Science (FSIS)", and Advancesoft Co., Ltd., has developed and released this software as "Advance/PHASE" (http://www.advancesoft.jp/).

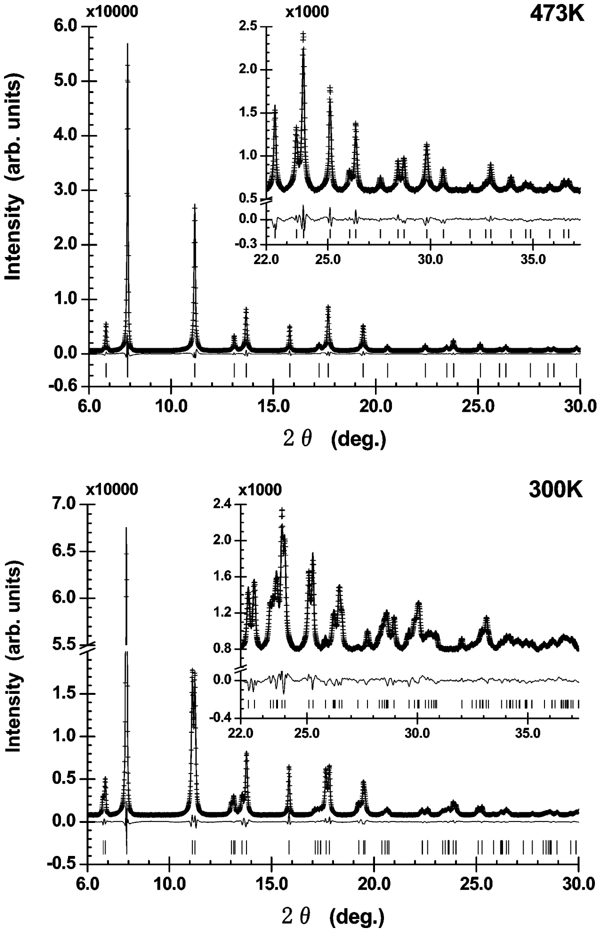


Figure 2. Observed (+) and calculated (gray line) X-ray diffraction profiles of the $Ge_{10}Sb_2Te_{13}$ high-temperature cubic phase at 473 K and low-temperature rhombohedral phase at RT (300 K). A difference curve (observed − calculated) appears at the bottom of each panel, and under the curve, vertical spikes indicate the reflection markers.

Table 1. Refined Structural Parameters for the $Ge_{10}Sb_2Te_{13}$ (GeTe/Sb_2Te_3 = 10:1) Rhombohedral Structure at RT (300 K) and Cubic Structure at 473 K[a]

300 K

	site	*g*	*x*	*y*	*z*	*B* (Å^2)
$Ge_{10/12}Sb_{2/12}$	1:1 (a)	0.924(3)	0.5176(2)	*x*	*x*	2.56(4)
Te	2:1 (a)	1.0	0	0	0	1.25(2)

473 K

	site	*g*	*x*	*y*	*z*	*B* (Å^2)
$Ge_{10/12}Sb_{2/12}$	4 (b)	0.908(3)	1/2	1/2	1/2	3.96(4)
Te	4 (a)	1.0	0	0	0	1.61(2)

[a] The space groups are $R3m$ and $Fm\bar{3}m$, respectively. Standard deviations are shown in parentheses. The final *R* factors and lattice parameters for the rhombohedral phase are R_{wp} = 4.05%, R_p = 2.89%, R_I = 0.92%, R_{wp} expected = 2.72%, a = 4.2582(2) Å, and α = 59.223(4)°, and those for the cubic phase are R_{wp} = 5.51%, R_p = 3.73%, R_I = 1.68%, R_{wp} expected = 3.24%, and a = 6.0028 (5) Å.

Table 2. Interatomic Distances (Å) from a Central Te(1) to Its Coordination Atoms in the Cluster Model of the GeTe Rhombohedral Phase at Room Temperature[a]

Ge(1)	×3	2.8088(17)	Sn(1)	×6	3.1565	Sb(1)	×6	3.1379
Ge(2)	×3	3.1829(17)						
Te(2)	×6	4.1710(22)	Te(2)	×12	4.4640	Te(2)	×12	4.4376
	×6	4.2708(5)						
Ge(3)	×1	4.9730(17)	Sn(2)	×8	5.4672	Sb(2)	×6	5.4349
	×3	5.0286(23)						
	×3	5.2467(21)						
Ge(4)	×1	5.6085(17)						

[a] Standard deviations are shown in parentheses. The final R factors for the Rietveld analysis were R_{wp} = 5.57% and R_I = 1.10%. The lattice constants and structural parameters obtained are indicated in the text. The interatomic distances in the models of the SnTe and (hypothetical) SbTe cubic structures are shown together with GeTe.

Figure 3a, consists of four blocks. The #1 band lies at the lowest energy in the figure, and #4 is located at the highest energy beyond the Fermi level (HOMO, highest-occupied molecular orbital), indicated by 0 eV. The other electron density analysis, the molecular orbital calculation, was performed using the DV-Xα method (discrete variational Hartree−Fock−Slater method) by placing a Te atom at the center and configuring a cluster of $N = 27$ (13Te + 14Ge) atoms (see Table 2), covering up to the fifth coordination shell. The program used was SCAT.[16] Atomic orbitals in a solid mutually interact to form molecular orbitals. These orbitals attain Bloch functions in the periodicity of a crystal lattice.[17] The calculation results are shown in Figure 3b, setting the Fermi level at 0 eV. By means of the diagrams in the figure, we can examine the contribution of the atomic orbitals to the generated molecular orbitals. 5*N* molecular orbitals were formed between −15 and 0 eV. By comparing these diagrams with Figure 3a, one can see that the #1 and #2 bands on the lower-energy side are formed mainly by the Te 5s and Ge 4s and by the Te 5p and Ge 4s atomic orbitals, respectively, while the higher-energy #3 and #4 bands are constructed chiefly by Te 5p and Ge 4p. (Waghmare et al.[18] demonstrated that this Te 5p and Ge 4s bonding interaction is related to structural distortion from the cubic to the rhombohedral phase). Ge 3d and Te 4d electrons (not included in Figure 3b) are distributed from −40 eV to −25 eV, making no contribution to the molecular orbital over −15 eV. Interaction between atomic orbitals generates bonding and antibonding molecular orbitals. The proportion at which electrons in atomic orbitals contribute to molecular orbitals (covalent bonds) can be calculated, using the molecular orbital method, as the overlap population. The overlap population diagram calculated for atomic pairs consisting of Te(1) and six nearest-neighbor Ge(2) and Ge(3) atoms (see Table 2) is shown in Figure 4a. The overlap population in molecular orbitals below −15 eV was almost zero. This figure indicates that the crystal is chemically bound, for the most part, by the *bonding* molecular orbitals in the three bands below the Fermi level shown in Figure 3a, which are formed by the outermost s and p electrons of the two kinds of atoms. The #4 band above the Fermi level mainly comprises *antibonding* molecular orbitals. The outermost electrons in Ge of Group IV and Te of VI elements are four and six, respectively. We can therefore reach the conclusion that (a) most of the 5*N* outermost electrons occupy these bonding orbitals, which gives this GeTe crystal

---

(16) Adachi, H.; Tsukada, M.; Satoko, C. *J. Phys. Soc. Jpn.* **1978**, *45*, 875.
(17) Hoffmann, R. *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures*; VCH Publishers: New York, 1988.
(18) Waghmare, U. V.; Spaldin, N. A.; Kandpal, H. C.; Seshadri, Ram. *Phys. Rev. B* **2003**, *67*, 125111.

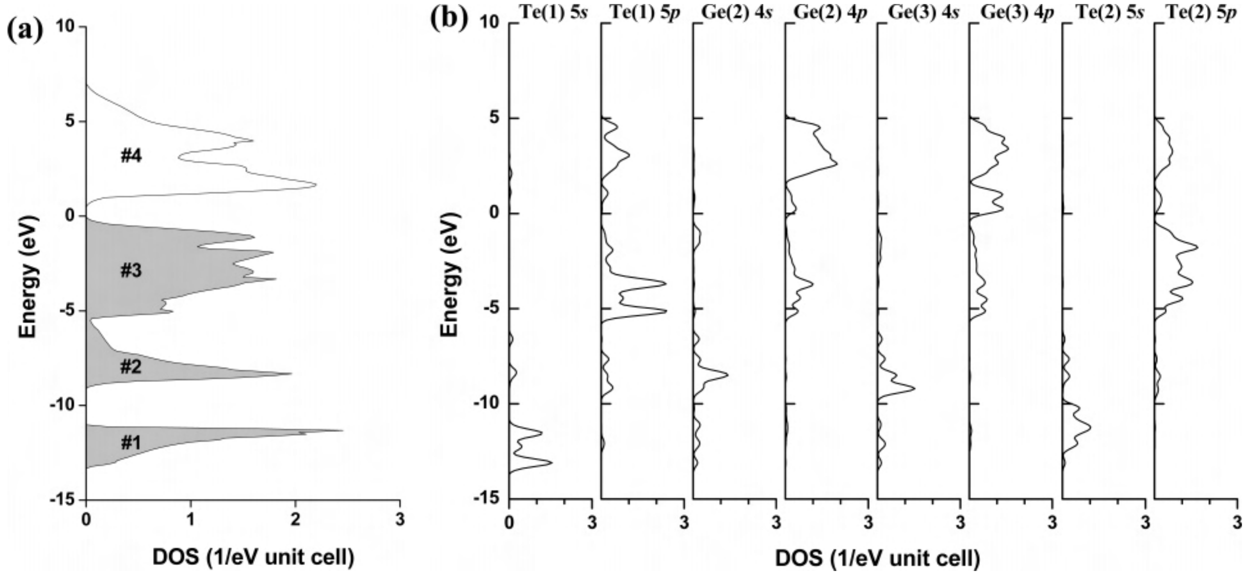


Figure 3. Density of state (DOS) diagrams for GeTe obtained by (a) the band and (b) the molecular orbital calculations. Shadowed regions in the left panel show valence bands occupied by electrons up to the Fermi level, which corresponds to 0 eV.

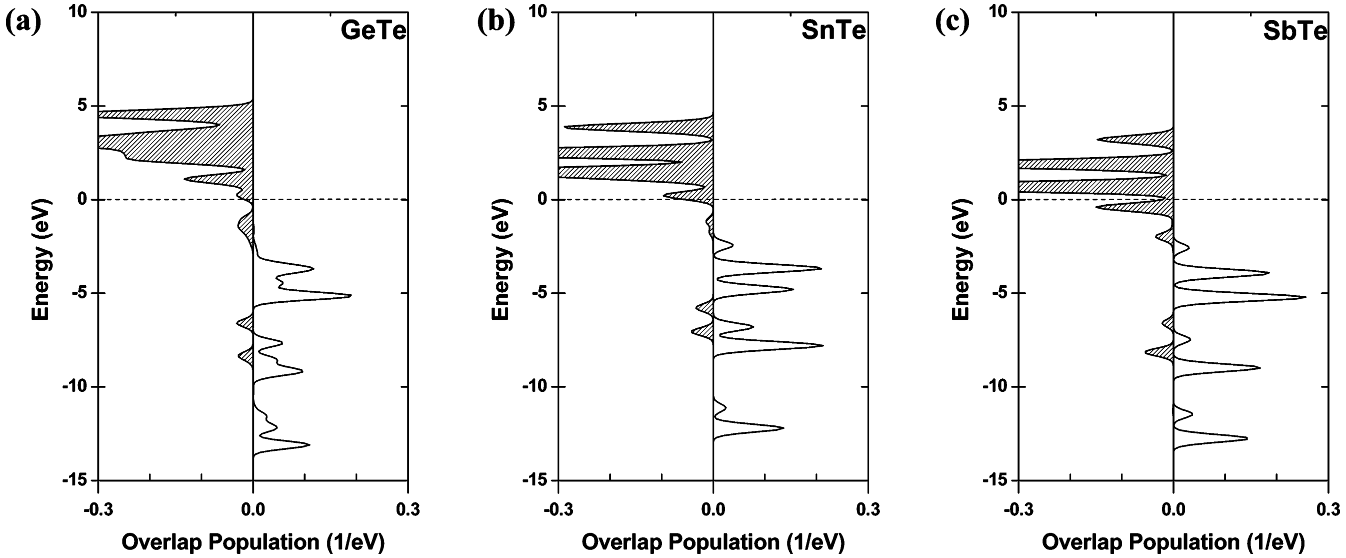


Figure 4. Overlap population diagrams calculated by the molecular orbital method with respect to the interaction between the central atom, Te(1), and the six nearest neighbors of each compound (see Table 2). Positive (right) and negative (left) sides of the diagram represent the population in the bonding and antibonding orbitals, respectively.

chemical stability and (b) the bondings with adjacent atoms by three orthogonal p orbitals on the outermost shell force their atomic configuration into an NaCl-type structure with octahedra formed by its six nearest neighbors. It is well-known that many IV−VI compounds, such as PbS (a = 5.9362 Å), PbSe (a = 6.1243 Å), PbTe (a = 6.454 Å), and SnTe (a = 6.313 Å), crystallize into this type of structure. The cell constants shown in parentheses were taken from *Crystal Structures* by Wyckoff.[19] It has been considered that in these crystals, the six outermost p electrons of the two adjacent IV and VI atoms mutually compensate for insufficient p orbitals through their resonance and that, as stated above, bondings with neighbors by these orbitals characterize the atomic arrangements of these compounds.[20] We have carried out the two kinds of calculations on these materials. Figures 5a and b and 4b, show, as an example, the electronic structures obtained for SnTe (These figures correspond to Figures 3a and b and 4a, respectively). This molecular orbital calculation indicates, as seen in Figure 5b, a certain electron density (Sn(2) 5p) at the Fermi level, obtained from the Sn−Te cluster. This is probably because the calculation was based on a tiny cluster of finite size. The smaller the cluster, the larger its surface area-to-volume ratio. In other words, the outer atoms of the cluster are more readily influenced because they are on the surface. We assume that the electron density at the Fermi level appears because of the molecular orbitals formed on the surface of the cluster. We can, however, see

---

(19) Wyckoff, R. W. G. *Crystal Structures*, Vol. 2, Krieger: Melbourne, FL, 1986.

(20) Abrikosov, N. Kh.; Bankina, V. F.; Poretskaya, L. V.; Shlimova, L. E.; Skudnova, E. V. *Semiconducting II−VI, IV−VI, and V−VI Compounds*; Plenum: New York, 1969.

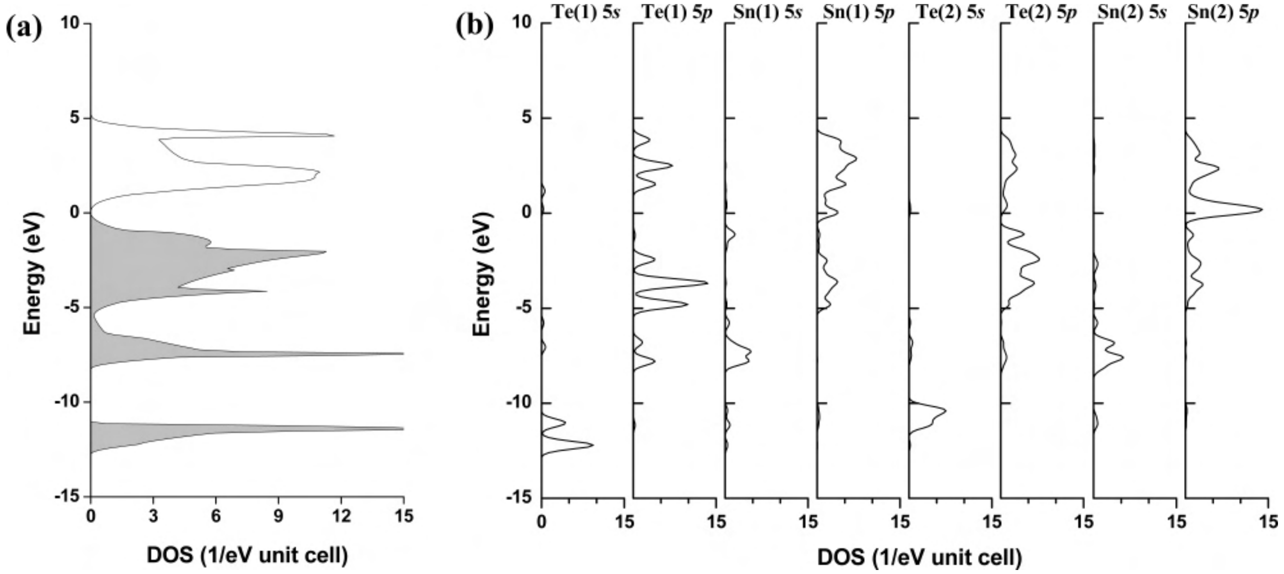


Figure 5. DOS diagrams for SnTe obtained by (a) the band and (b) the molecular orbital calculations. The second band from the bottom is formed mainly by Te 5p and Sn 5s atomic orbitals respectively, while the third is constructed chiefly by Te 5p and Sn 5p, almost the same as in the case of GeTe.

almost the same result as in the case of GeTe discussed above. The net (effective) charge, which means the number of excess electrons that VI atoms have received from IV atoms in a cluster, calculated for Ge and Te atoms of $N = 27$, was about 0.3_0 per single atom, showing that this cluster tolerates ionic bonding nature. Those for PbS, PbSe, PbTe, and SnTe were about 0.4_6, 0.2_8, 0.3_8, and 0.2_8, respectively. This difference in electronegativity between the two kinds of atoms is presumed to be another major reason that these compounds have an NaCl-type atomic arrangement, which frequently appears in AB ionic crystals.

Intrinsic Vacancies in the $GeTe-Sb_2Te_3$ Pseudobinary Crystals. We now discuss the case of the $GeTe-Sb_2Te_3$ pseudobinary compound ($x > 0$). An Sb atom, which is a Group V element, has three p electrons, meaning that it has one excess p electron compared with Ge. Therefore, in the $GeTe-Sb_2Te_3$ pseudobinary compound, when the number of vacancies appearing in the Na sites has reached half the number of the substituted Sb atoms, the stable structure in which outermost electrons occupy almost only the bonding molecular orbitals, namely the closed shell structure of the p orbitals can be preserved, as in the case of GeTe. Here, note that one vacancy compensates for two excess p electrons. (The total number of p electrons of two Sb atoms is equal to that of three Ge electrons.) In other words, it can be considered that when the composition of the pseudobinary compound is expressed as $(GeTe)_{1-x} + (Sb_2Te_3)_x$ ($0 \leq x \leq 1$), the fraction of the vacancies in the Na sites $v(x)$ changes continuously according to $x/(1 + 2x)$. As shown in Figure 6, the composition dependence of the vacancy fraction can be observed by plotting the g values obtained by the structural analyses (see Table 1). For $Ge_2Sb_2Te_5$ (2:1), each of the three different specimens was subjected to diffraction measurements and structural analyses. The standard deviation was estimated, from these three pieces of data, to be ± 0.013. The error bar displayed in the diagram shows the standard deviation. The standard deviation was also estimated in the same way for the volume changes described below. By comparing $g(x)$ with the $1 - v(x)$ curve in the figure, one can see that the vacancy rate varies following $v(x)$ within the estimated error range. The molecular orbital calculation for a cluster ($N = 33$, center atom Te; the structural parameters used for the calculation were taken from reference[8]) with the Sb_2Te_3 15-layer structure showed that 0.1_8 electrons per single atom move from Sb to Te. This means that the electronegativity of Sb is lower than that of Te, the same as in the case of GeTe, which supports the experimental result that, in this pseudobinary NaCl-type crystal, Ge and Sb atoms occupy a common site (Na site) to form one of the two kinds of face-centered sublattices and that Te atoms compose the other.

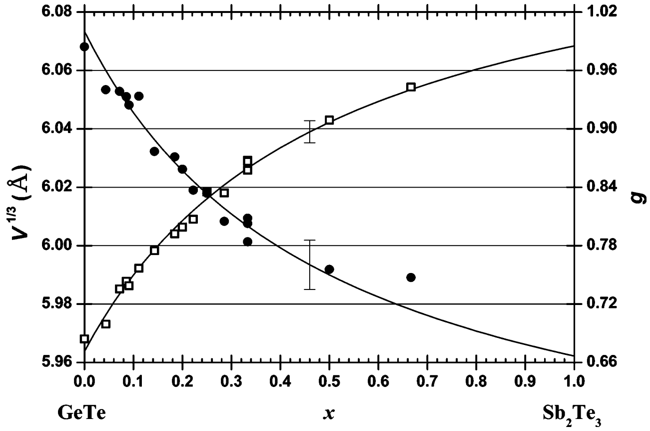
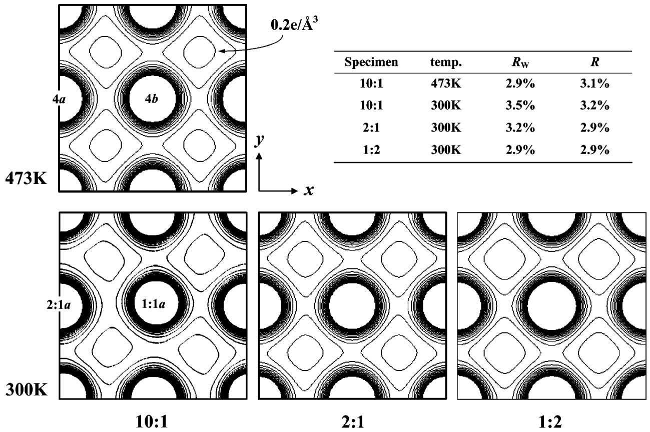


Figure 6. Composition dependence of the g parameter, which indicates the site occupancy of Ge + Sb atoms at Na sites (●) and that of the cubic root unit cell volume ($V^{1/3}$) (□). The horizontal axis, x, indicates the fraction of Sb_2Te_3 in the $GeTe-Sb_2Te_3$ pseudobinary system. The errors were estimated using the g and $V^{1/3}$ values obtained from three $Ge_2Sb_2Te_5$ ($x = 1/3$) specimens. The two curves in the figure are least squares fitting results obtained by taking vacancy contribution into account.

Figure 7 shows the electron density distributions provided by MEM (maximum entropy method)[21] analyses for some specimens. The program used for the calculation was



Specimen	temp.	R_W	R
10:1	473K	2.9%	3.1%
10:1	300K	3.5%	3.2%
2:1	300K	3.2%	2.9%
1:2	300K	2.9%	2.9%

Figure 7. Electron density maps for the GeTe/Sb_2Te_3 = 10:1 (RT and 473 K), 2:1 (RT), and 1:2 (RT) specimens in the *c* plane ($z = 1/2$) of the unit cell obtained by MEM. The 10:1 specimen at RT was in the low-temperature rhombohedral phase with a slightly deformed NaCl-type structure. The others were in the NaCl-type cubic phase. The contours are drawn at intervals of 0.1 from 0.0 to 2.0 e Å^{-3}. One side of each square frame corresponds to the respective lattice constants. The inset table shows the final R_W and R factors for the MEM analyses.

MEED.[22] The final R_W/R value is tabulated in the figure. For the 10:1 specimen, the crystal structure was analyzed not only at room temperature but also in the cubic phase at 473 K. These MEM maps demonstrate that the electron density distribution, or electronic structure, of NaCl-type structures that appear in the GeTe−Sb_2Te_3 pseudobinary system changes little according to composition. It can be assumed that the border between the atoms at the Na and Cl sites coincides with the trough of electron density between both sites. Examination of the MEM maps of all specimens, not just the four maps shown in Figure 7, has revealed that this trough is located at almost the middle point of the Na and Cl sites, regardless of the specimen composition or phase. This fact indicates that the mean atomic radius of Ge, Sb, and the vacancies that occupy the Na sites (r_{Na}) are nearly equal to the radius of Te in the Cl sites (r_{Cl}), and the value of r_{Na}/r_{Cl} shows minimal composition dependence in that it retains a constant value of almost unity. The NaCl-type structure is, as mentioned above, typical of an ionic crystal (A, cation; B, anion) of an AB binary compound. It is known that this structure appears around an area of $0.414 \leq r_A/r_B < 0.732$.[23] When the atomic radius ratio is within the area, the crystal has a spatially dense structure. However, the MEM analyses indicated that the radii of Ge/Sb + vacancy at the Na site and Te at the Cl site are almost equal. When $r_A \approx r_B$, the NaCl-type structure is spatially very sparse. These also suggest that the orthogonal p−p covalent bondings between atoms allow the metastable phase of the GeTe−Sb_2Te_3 pseudobinary system to adopt the NaCl-type atomic configuration.

The composition dependence of the cubic root unit cell volume ($V^{1/3}$) is shown in Figure 6 (V shows the unit cell volume of the cubic phase. In the rhombohedral phase, V corresponds to quadruple the unit cell volume.) When $Sb_2Te_3(x)$ increases, $V^{1/3}(x)$ gradually reduces its rate of increase, showing a marked departure from the linear change predicted by Vegard's law.[24] In the NaCl-type structure of GeTe−Sb_2Te_3, we learned that an extremely large number of vacancies are introduced into the crystal. These vacancies are likely to relieve the volume expansion rate accompanied by the increase in Sb_2Te_3. In fact, $V^{1/3}(x)$ has a strong correlation with the vacancy rate $\upsilon(x)$ as can be seen in Figure 6. The curve in the diagram is obtained by fitting $a + b\upsilon(x)$ using the least squares method, where $a = 5.964(1)$ and $b = 0.314(8)$ Å. Assuming that Ge atoms are replaced by the same number of Sb atoms without introducing any vacancies, it is expected that $V^{1/3}$ would vary linearly following Vegard's law, namely, $a + bx$. At $x = 1$, that is SbTe, $V^{1/3}$ is estimated to be 6.278 Å, which corresponds to 30.9 Å^3 as the mean volume per single atom. This would appear to be rather large (see Figure 6). In the actual Sb−Te binary system, however, the crystal structures of Sb_2Te_3[8] and Sb_2Te[25] have been already determined, and recently, in addition to these compounds, a series of intermetallic compounds which are expressed as $Sb_{2n}Te_3$ ($n = 1, 2, 3, ...$,) have been discovered.[26] The mean volumes for Sb_2Te_3, Sb_4Te_3, and Sb_2Te are 32.0[8], 31.1[26], and 31.0 Å^3,[25] respectively. The estimated volume, 30.9 Å^3, is in good agreement with these volumes. Figure 8a and b shows DOSs obtained by the above-mentioned two calculations for this hypothetical SbTe crystal. It was assumed that the crystal has an NaCl-type cubic structure. Almost the same DOS distributions were obtained as in the case of GeTe. However, the Fermi level lies in the #4 band. This is the result of the excess p-electron occupation of the antibonding molecular orbitals, as can be seen in these figures and in Figure 4c. We therefore conclude that in the actual NaCl-type structure, which appears extensively in the GeTe−Sb_2Te_3 pseudobinary system, a total of 10 of the outermost electrons provided by the adjacent two atoms, which are maintained by generating vacancies when Sb_2Te_3 increases, occupy almost only the bonding orbitals to stabilize the crystal and that the closed shell p−p bonding in the outermost electrons arranges their atomic configuration into an NaCl-type structure. Luo and Wuttig[27] have recently shown that, of the many kinds of binary and ternary chalcogenide compounds that have been examined for use as phase-change optical memory, only those compounds with cubic or NaCl-type structure can be applied to practical use; in their paper, these are called "successful" materials. The crystal structures of the unsuccessful materials are stabilized by sp^3 bondings; while N_{sp} (the average number of valence electrons per single atom) increases, the valence electrons of the successful materials favor p−p bondings, which prevent those electrons from occupying antibonding orbitals, namely the conduction band. The border between the successful and unsuccessful

---

(21) Takata, M.; Nishibori, E.; Sakata, M. *Z. Kristallogr.* **2001**, *216*, 71.
(22) Kumazawa, S.; Kubota, Y.; Takata, M.; Sakata, M.; Ishibashi, Y. *J. Appl. Crystallogr.* **1993**, *26* (3), 453.
(23) Vainshtein, B. K.; Fridkin, V. M.; Indenbom, V. L. *Structure of Crystals*; Springer-Verlag: Berlin, 1995.
(24) Cullity, B. D. *Elements of X-ray Diffraction,* 2nd ed.; Addison-Wesley: Reading, MA, 1978.
(25) Agafonov, V.; Rodier, N.; Céolin, R.; Bellissent, R.; Bergman, C.; Gaspard, J. P. *Acta Crystallogr. C* **1991**, *47*, 1141.
(26) Kifune, K.; Kubota, Y.; Matsunaga, T.; Yamada, N. *Acta Crystallogr. B* **2005**, *61*, 492.
(27) Luo, M.; Wuttig, M. *Adv. Mater.* **2004**, *16*, 5, 439.

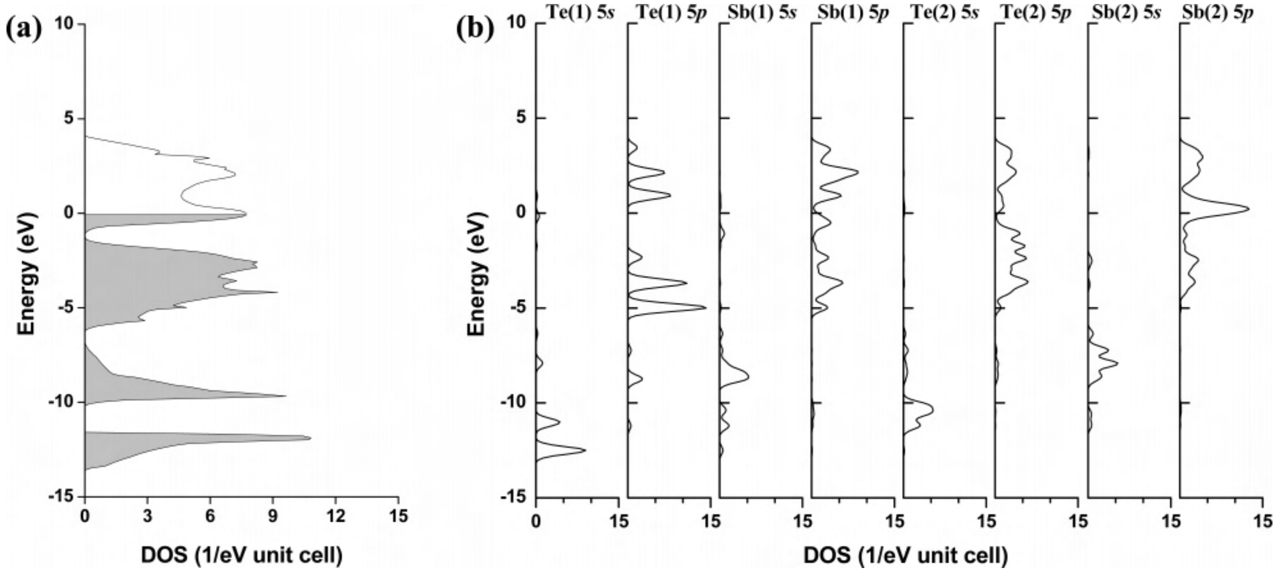


Figure 8. DOS diagrams for a hypothetical SbTe rock salt-type cubic structure obtained by (a) the band and (b) the molecular orbital calculations. It can be seen that the Fermi level lies in the conduction band.

materials is located at $N_{sp} = 4.25$. The GeTe−Sb_2Te_3 pseudobinary metastable compound is exactly applicable to this rule. This compound, which is one of the most commonly used recording materials today, as mentioned in the Introduction, maintains an N_{sp} of between 5.0 and 4.7 and a pseudo or cubic NaCl-type structure over a wide composition range from 100% at least to 33 at. % GeTe. The structure is stabilized by the p−p bonds formed by the electrons that almost exclusively occupy the valence band. However, this NaCl-type structure becomes unstable with increased Sb_2Te_3. For example, when the $GeSb_4Te_7$ (1:2) film that has crystallized into an NaCl-type structure is left at room temperature for several hours to several days, a structural transformation to the stable phase (12-layer structure) begins to appear. In Sb_2Te_3, the presence of an NaCl-type structure has not yet been confirmed.

Conclusion

All of the amorphous films of the GeTe($1-x$)−Sb_2Te_3(x) pseudobinary compounds ($0 \leq x \leq 2/3$), which are obtained by substituting Sb_2Te_3 for GeTe, have been crystallized into simple NaCl-type structures, regardless of their compositions, through instantaneous laser irradiation. When the ratio of Sb_2Te_3 increases, vacancies are *intrinsically* generated, which ensure that valence electrons provided by adjacent Ge/Sb and Te atoms remain constant to preserve crystal chemical stability.

It has been found or predicted that not only in GeTe−Sb_2Te_3 but also in pseudobinary compounds such as GeTe−As_2Te_3 or GeTe−Bi_2Te_3, a series of intermetallic compounds with long-period stacking structures similar to GeTe−Sb_2Te_3 are formed in thermal equilibrium.[28,29] Other than these compounds, in IV−VI compounds with an NaCl-type or similar structure, it is expected that when a Group IV element is replaced by a Group V element, the NaCl-type structure which inevitably contains an enormous number of vacancies appears as a stable or metastable phase over a wide composition range, as is the case for the GeTe−Sb_2Te_3 pseudobinary compound. This is a potentially interesting research subject.

Acknowledgment. The synchrotron radiation experiments were performed on BL02B2 at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2004B0356-ND1c-np). We express our sincere thanks to Mr. K. Katoh at JASRI for his kind advice on the experiment and analysis.

IC051677W

---

(28) Shu, H. W.; Jaulmes, S.; Flahaut, J. *J. Solid State Chem.* **1988**, *74*, 277.
(29) Shelimova, L. E.; Karpinskii, O. G.; Konstantinov, P. P.; Avilov, E. S.; Kretova, M. A.; Zemskov, V. S. *Inorg. Mater.* **2004**, *40*, 5.