

Crystal structure and its thermal behavior of $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ ($\text{GeTe}:\text{Sb}_2\text{Te}_3 = 8:1$), a suitable material for high-speed and high-density phase-change recording

Toshiyuki Matsunaga* and Noboru Yamada†

*Characterization Technology Group, Matsushita Technoresearch, Inc.

†Storage Media Systems Development Center, Matsushita Electric Industrial Co., Ltd.
3-1-1 Yagumo-Nakamachi, Moriguchi, Osaka 570-8501, Japan

ABSTRACT

The crystal and electronic structures of $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$, a $\text{GeTe}(1-\mathbf{x})\text{-Sb}_2\text{Te}_3(\mathbf{x})$ pseudobinary compound, were examined in detail by powder X-ray diffraction and molecular orbital methods. This compound has a high-temperature cubic phase (an NaCl-type structure) and a low-temperature rhombohedral phase (a slightly distorted NaCl-type structure). In these crystals, the *s* and *p* outermost orbitals are responsible for bonding with adjacent atoms and these orbitals form a conduction band in the crystal. The conduction electrons make the crystalline (erased) area in an optical recording film metallic and opaque to visible and near-visible light. The electron density rises with decrease of the pseudobinary composition, \mathbf{x} , which leads to emphasis of the difference in optical properties between the amorphous and crystalline phases.

Keywords: Blu-ray, phase-change optical disc, $\text{GeTe-Sb}_2\text{Te}_3$ pseudobinary compounds, GeTe-rich composition, outermost *s* and *p* orbitals, conduction band, opacity, free electron density.

1. INTRODUCTION

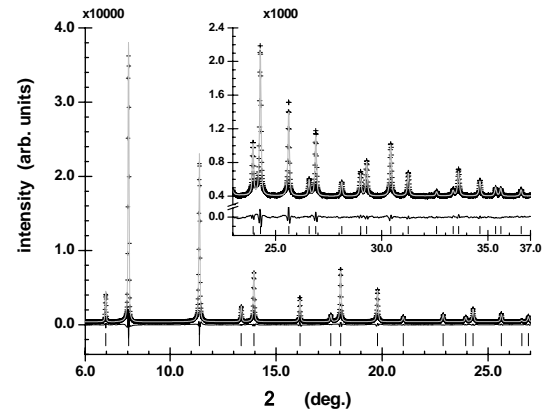
Optical recording discs are now in extensive use as rewritable nonvolatile high-density memory storage media, for computers and particularly for home-use videodisc recorders. The most widely used recording material today is $\text{GeTe-Sb}_2\text{Te}_3$. This is because it has three characteristics essential for DVD-RAMs (digital versatile disc – random access memory): (1) records can be rewritten very fast, (2) records can be rewritten at least 10^4 times, and (3) records can be retained stably for extended periods.

The most important property of any recording medium is to record as much information as possible as fast as possible. To meet this requirement in phase-change optical recording media, Blu-ray discs, on which as much as 50 GB of information can be recorded by blue-violet laser, have been rapidly developed and finally placed on the market on July 23 this year. The recording film is becoming steadily thinner to realize higher density and faster recording: in the Blu-ray disc, the film thickness is now only several nanometers. A typical material used in current optical discs is $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($\text{GeTe}:\text{Sb}_2\text{Te}_3 = 2:1$). For this type of 2:1 composition, as well as the 1:1 composition, the crystal structures and the relation between structures and high-speed phase-change characteristics have been investigated in detail¹⁻⁴. On the other hand, in Blu-ray discs, such GeTe-rich pseudobinary compounds as $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ (8:1) are adopted, which enable sufficient optical changes even in very thin films just a few nanometers thick. For these GeTe-rich compounds, however, the details of crystal structures and their temperature dependencies, and chemical bonding natures, which are believed to have a close relation with their optical characteristics, have been little examined. We then investigated in detail the crystal structure and its temperature dependency in $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ by powder X-ray diffraction using a synchrotron radiation facility and examined the chemical bonding nature by molecular orbital calculation.

Table I. Refined structural parameters for the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ high-temperature phase at 423 K. Standard deviations are shown in parentheses. The final R -factors and lattice parameter are $R_{\text{wp}} = 4.57\%$, $R_{\text{p}} = 3.18\%$, $R_{\text{I}} = 2.39\%$, $R_{\text{wp}} \text{ expected} = 4.02\%$ and $a = 6.0055(2) \text{ \AA}$.

atom	site	g	x	y	z	$B(\text{\AA}^2)$
$\text{Ge}_{8/11}\text{Sb}_{2/11}$	4(b)	0.995(3)	1/2	1/2	1/2	3.75(3)
Te	4(a)	1.0	0	0	0	1.57(2)

Fig. 1. (→) Observed (+) and calculated (grey line) X-ray diffraction profiles of the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ high-temperature phase at 423 K. A difference curve (observed–calculated) appears at the bottom of each Figure, and under the curve, the reflection markers are indicated by vertical spikes.



2. EXPERIMENTAL

The specimen for diffraction measurement was made using the following method. First, a thin film of $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ with a thickness of about 3000 \AA was sputtered onto a glass disc with a diameter of 120 mm. Inductively coupled plasma atomic emission spectrometry (ICP) confirmed that the composition of the specimen was close to $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$. The film was crystallized (initialized) by laser irradiation. The film was then powdered by scraping with a spatula. The powder was packed in quartz capillary tube with an outer diameter of 0.2 mm for use in the diffraction experiment. To insulate against the atmosphere, the opening of the capillary was sealed by melting with an oxyacetylene flame.

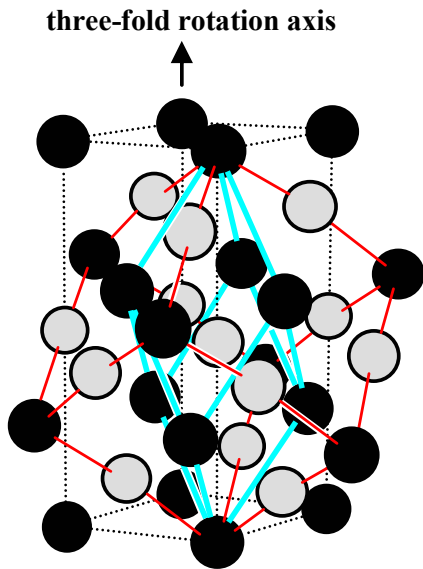


Fig. 2. Structure of $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ low-temperature phase shown in both the rhombohedral (thick blue lines) and hexagonal (dotted lines) unit cells. Gray circles show Ge or Sb; black circles indicate Te. NaCl-type structure of the high-temperature phase, shown by thin red lines, is deformed due to the transition to the low-temperature phase.

The diffraction experiment was performed using the BL02B2 beam line at the Japan Synchrotron Radiation Research Institute (SPring-8)⁵. The incidence X-ray beam was highly monochromatic and parallel by employing a precollimator mirror and a double-crystal monochromator. The X-ray energy was 29.417 keV ($\lambda = 0.42146 \text{ \AA}$). Diffraction intensity was measured using a Debye-Scherrer camera with a radius of 278 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 method⁶. The program used was RIETAN⁷. The neutral atomic scattering factors were used for all of Ge, Sb, and Te atoms. The atomic thermal vibration was assumed to be isotropic. 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 energy of the synchrotron radiation used was confirmed by recording the diffraction intensity of CeO_2 ($a = 5.4111 \text{ \AA}$) powder as a reference specimen at room temperature under the same conditions.

3. RESULTS

The laser crystallized $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ film was, different from the cases of $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (2:1) and GeSb_2Te_4 (1:1), not an NaCl-type cubic structure but a rhombohedral structure at room temperature. The mean crystallite size was about 15nm obtained by the Wilson plot⁸. When this rhombohedral crystal is heated, however, the structure transformed to an NaCl-type cubic structure at around 395 K. Once the structure had changed, the high-temperature phase maintained a uniform structure up to around the melting point.

3.1. High-temperature phase structure

Table I and Figure 1 show the results of a structural analysis of the high-temperature phase whose structure belongs to the space group $Fm\bar{3}m$ ⁹ of the three elements, Te atoms occupy 100% of the 4(a) sites while Ge and Sb atoms are located randomly at the 4(b) sites, forming an NaCl-type structure (see Fig. 8). However, not all the 4(b) sites are occupied by atoms, leaving about 9 at. % vacancies. The content of the vacancies was almost invariable, regardless of the temperature. In this phase, every atom has six nearest neighbours at equal distances. The interatomic distance of all atomic pairs present in the crystal is half the lattice constant $a(T)$. This phase can be described in hexagonal notation as a six-layered structure ($a = 4.2465$, $c = 10.402$ Å, at 423 K).

3.2. Low-temperature phase structure

At room temperature, $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ ($\mathbf{x}=1/9$) film crystallizes into a rhombohedral structure ($R3m$ ⁹) in which a NaCl-type structure is slightly distorted by laser annealing along one of the three-fold rotation (-inversion) axes (Fig. 2). This structure is different from the $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ($\mathbf{x}=1/3$) stable phase ($P\bar{3}m1$ ⁹, $a = 4.2247$, $c = 17.239$ Å, at RT)⁴, which is an isostructure of the low-temperature phase of GeTe ($\mathbf{x}=0$)¹⁰. As shown in Fig.

Table II. Refined structural parameters for the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ low-temperature phase at 92K. Standard deviations are shown in parentheses. The final R -factors and lattice parameter are $R_{\text{wp}} = 4.69$ %, $R_{\text{p}} = 3.09$ %, $R_{\text{l}} = 1.31$ %, R_{wp} expected = 3.54 % and $a = 4.2473$ (2) Å, $\alpha = 59.317$ (3) °.

atom	site	g	x	y	z	$B(\text{Å}^2)$
$\text{Ge}_{8/11}\text{Sb}_{2/11}$	1(a)	1.047(3)	0.5180(2)	x	x	1.80 (4)
Te	1(a)	1.0	0	0	0	0.50 (2)

Fig. 4. (→) Observed (+) and calculated (grey line) X-ray diffraction profiles of the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ high-temperature phase at 92K. A difference curve (observed–calculated) appears at the bottom of each Figure, and under the curve, the reflection markers are indicated by vertical spikes.

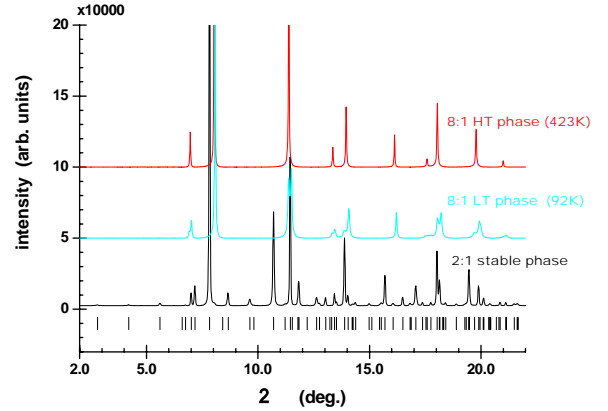
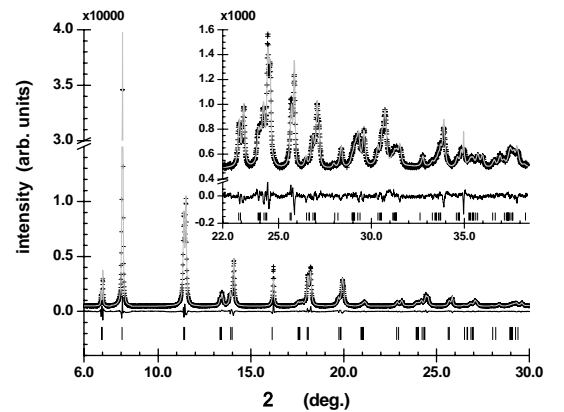


Fig. 3. Powder X-ray diffraction profiles of $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ (8:1) at high- and low-temperature phases and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (2:1) stable phase, obtained by synchrotron radiation (29.5keV) of SPring-8. Under the curves, the reflection markers for the 2:1 stable phase are indicated by vertical spikes.



3, the diffraction patterns of the former high- and low-temperature phases are similar to each other, whereas the latter stable phase is fairly complicated because its c -axis is longer than the other two. Our structural analysis results for the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ low-temperature phase are shown in Table II and Fig. 4. In this phase, Te and Ge/Sb layers in the cubic close-packed structure of the high-temperature phase—in other words, slightly distorted face-centred cubic sublattices formed by Te and Ge/Sb—are shifted from each other by approximately $\sqrt{3}/2\Delta x$ in the [111] direction (the c axis direction in hexagonal notation); therefore, there exist three shorter interatomic distances (r_s) and three longer (r_l) between the central atom and its six neighbors. Here, Δx is the shift parameter from the equilibrium position in the high-temperature phase ($\Delta x = 0.018$ at 92 K; see Table II).

3.2. Crystalline phase transformation properties

Figure 5 shows the temperature (T) dependence of unit cell volume ($V^{1/3}$), which changes continuously with T , while $\partial(V^{1/3})/\partial T$ has discontinuity at around

385 K, which is presumably the transition temperature between the two phases. In the respective low-temperature and high-temperature phases, however, $V^{1/3}$ varies almost linearly by temperature, and their linear expansion coefficients are $4.21 \times 10^{-5}/\text{K}$ and $6.69 \times 10^{-5}/\text{K}$, respectively. The temperature dependencies of r_s and r_l are shown in Fig. 5. At the low temperature of 92 K, $r_s = 2.882$ and $r_l = 3.102 \text{ \AA}$. However, as the temperature rises, r_s/r_l gradually approaches unity toward the transition temperature.

Figure 6 shows the dependency of isotropic temperature factors in the Ge/Sb and Te sites at high

temperatures. Since the average atomic weight of Ge/Te is smaller than that of Te, when compared at the same temperature, the thermal vibration of the former is more intense than the latter. At 700–800 K where erasure (the phase change from an amorphous to a crystalline state) is performed, atoms, especially Ge/Sb, intensely oscillate thermally. Mean atomic displacement due to thermal vibration is around 0.26 \AA at 773 K, which is approximately 9% of the nearest interatomic distance.

4. DISCUSSION

In NaCl-type structures of the $\text{GeTe}(1-x)\text{-Sb}_2\text{Te}_3(x)$ pseudobinary system, outermost s and p orbitals are responsible for bonding with adjacent atoms. These atomic orbitals form molecular orbitals by mutual interaction, and the molecular orbitals together create a conduction band. This is why this substance has metallic

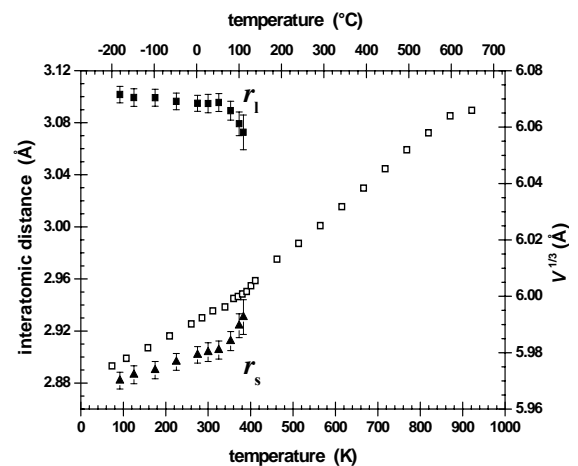


Fig. 5 Temperature dependence of the cubic square unit cell volume ($V^{1/3}$) shown by open squares. The estimated errors are smaller than the marks. Painted squares and triangles represent shorter and longer interatomic distances, r_s and r_l , with respect to the Ge/Sb - Te bonds in the low-temperature phase, respectively.

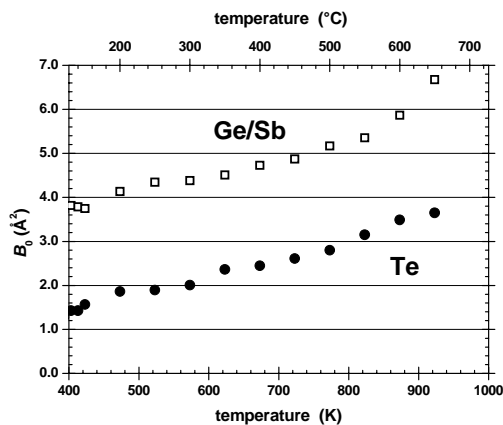


Fig. 6 Temperature dependence of the isotropic temperature factor B_0 for the Ge/Sb and Te sites, shown by squares and circles, respectively. The estimated errors are smaller than the marks.

properties and is opaque to visible light, including red and blue-violet. The density of the conduction electrons increases with the binary composition x , so GeTe-rich GeTe-Sb₂Te₃ pseudobinary film can obtain sufficient optical change even if in an extremely thin layer.

4.1. Charge density analyses by x-ray diffraction measurements

Figure 7 shows the electron density distribution in the high-temperature phase (423 K, $a = 6.0055(2)$ Å) obtained by MEM (Maximum Entropy Method) analysis¹¹. The program used for the calculation was MEED¹². Final weighted and non-weighted R -factors were $R_w = 3.1\%$ and $R = 2.9\%$. As seen in this Figure, electron localization showing strong covalent bonding is rarely observed between atoms. Although a difference Fourier synthesis was performed, the presence of positive or negative charge that would suggest a strong ionic bond nature, like Na^+Cl^- , was not observed in either the 4(a) or the 4(b) sites. As the MEM map shows, the electron density of each atom is spherically symmetrical, and electrons are distributed at relatively high density even in the interatomic space. In the unit cell of this crystal, the position that is the most distant from all atoms is the 8(c) site. At this position, electron density was about 0.16-0.17 $e/\text{Å}^3$. This density is assumed to correspond to the free (conduction) electron density in the crystal. Our results suggest that this compound (the high-temperature phase) can be regarded as a substance with metallic-type bonds. The electronic state in the crystal was examined by molecular orbital calculation.

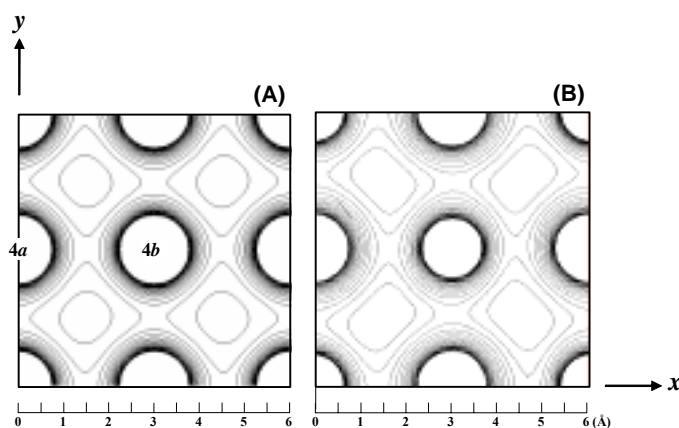


Fig. 7 Electron density maps for the Ge₈Sb₂Te₁₁ (A) high-temperature (at 423 K) phase in the c -plane ($z = 1/2$) of the unit cell obtained by MEM. (B) shows that calculated for the GeTe high-temperature phase on the same plane as the MEM map using the molecular orbital (DV- $X\alpha$) method. The contours are drawn at intervals of 0.01 from 0.0 to 0.2 $e/\text{Å}^3$.

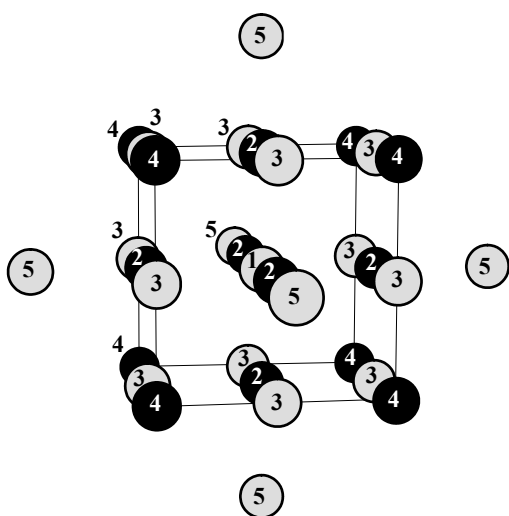


Fig. 8. A cluster model used for the molecular orbital (DV- $X\alpha$) calculation. The cluster consists of 19 Ge and 14 Te atoms indicated by gray-painted and black circles, respectively. The numerals show the groups to which the coordination atoms belong. The central atom is Ge(1): the longest interatomic distance is 6.0055 Å (at 423 K) between Ge(1) and Te(5). The thin lines indicate the face-centered cubic unit cell of the NaCl-type high-temperature phase.

was performed, the presence of positive or negative charge that would suggest a strong ionic bond nature, like Na^+Cl^- , was not observed in either the 4(a) or the 4(b) sites. As the MEM map shows, the electron density of each atom is spherically symmetrical, and electrons are distributed at relatively high density even in the interatomic space. In the unit cell of this crystal, the position that is the most distant from all atoms is the 8(c) site. At this position, electron density was about 0.16-0.17 $e/\text{Å}^3$. This density is assumed to correspond to the free (conduction) electron density in the crystal. Our results suggest that this compound (the high-temperature phase) can be regarded as a substance with metallic-type bonds. The electronic state in the crystal was examined by molecular orbital calculation.

4.2. Bonding nature elucidation by a molecular orbital method

As described at the beginning of this article, pseudobinary (GeTe)_{1-x} - (Sb₂Te₃)_x film crystallizes into a NaCl-type structure as a result of laser annealing over a wide composition range from GeTe ($x = 0$) to GeSb₂Te₄ ($x = 1/2$). To simplify the calculation, the structure is assumed to be GeTe instead of Ge₈Sb₂Te₁₁ ($x = 1/9$). Actual recording film is only several nanometres thick, and the mean lateral size of the crystallites in the film is approximately 10 to 20 nm^{1,3}. On this type of aggregate of microcrystallites, it is likely that the electronic state can be described more accurately using the molecular orbital

method, which uses an atomic cluster with finite size (microcrystallite) than by using band calculations, which assume infinite periodicity of the crystal lattice. The lattice constant used for the calculation was $a = 6.0055 \text{ \AA}$, which corresponds to the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ structure at 423 K. The program used was SCAT¹³. The calculation was performed by placing a Ge atom at the center and configuring a cluster of 33 atoms (Fig. 7), covering up to the fifth nearest neighbors ($r = 6.0055 \text{ \AA}$). The computed result was very close to the electron density distribution obtained by MEM analysis (see Fig. 8), showing that the electron densities of the GeTe and $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ high-temperature phases were expressed correctly by both MEM analysis and molecular orbital calculation.

Atomic orbitals in a solid mutually interact to form molecular orbitals. The density of state obtained by the calculation is shown in Fig. 9, setting the Fermi level at 0 eV. The band seen on the energy side lower than -6.5 eV is formed mainly by Ge 4s and Te 5s orbitals, while the higher energy band is formed by Ge 4p and Te 5p orbitals. This band is filled with electrons as far as the central portion. In other words, electrons penetrate up to halfway into the conduction band, so this substance (an aggregate of microcrystallites) must have metallic properties. In fact, it has been suggested that the $\text{GeTe-Sb}_2\text{Te}_3$ pseudobinary compound film, which crystallizes under laser irradiation into a metastable state (the NaCl-type structure), is a metallic substance, from the relationship between melting point and thermal expansion coefficient and measurements of specific resistivity¹⁴. Sb atom's outermost s and p orbitals are also expected to bond with adjacent atoms to form a conduction band in a crystalline state.

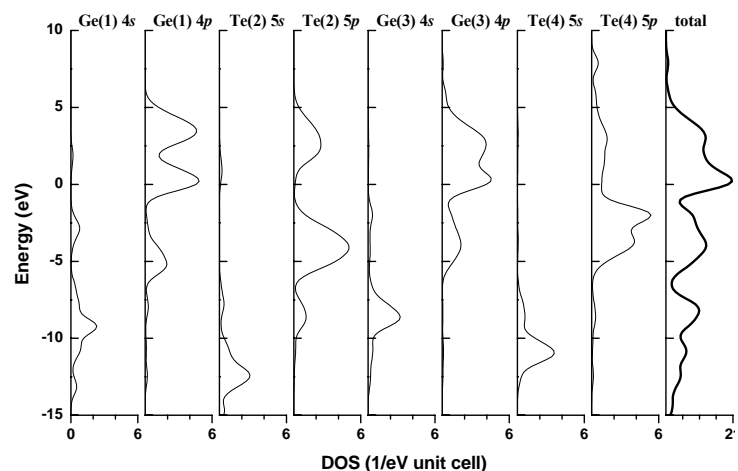


Fig. 9. Density of state (DOS) diagrams obtained by the molecular orbital (DV-X α) calculation for the NaCl-type cubic structure of the high-temperature phase.

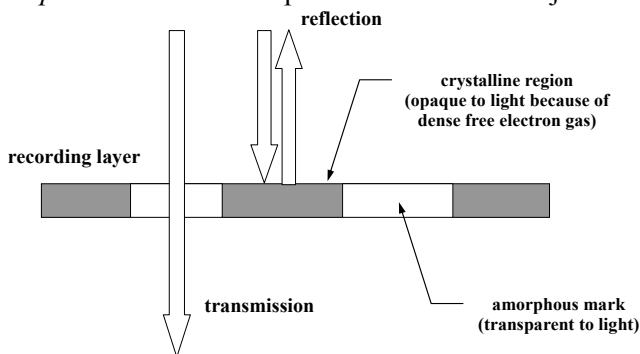


Fig. 10. An optical disc records information during the phase transformation between amorphous and crystalline states of the material by such changes in its optical characteristics as transmissivity or reflectivity. The amorphous state is transparent to light; on the other hand, the crystalline state is opaque because of the presence of an enormous number of free electrons.

4.3. Why $\text{GeTe-Sb}_2\text{Te}_3$ microcrystallite is opaque to light

Above discussions have suggested that Ge, Sb, and Te atoms in $\text{GeTe-Sb}_2\text{Te}_3$ pseudobinary compounds provide four, five, and six electrons, respectively, in the conduction band; an enormous number of free (conduction) electrons are present in the crystal that can migrate freely in space as gases, presumably a major factor for their opaqueness (see Fig. 10). If the effective mass of a conduction electron is assumed to be equal to that of a free electron, the plasma wavelength should be about 100 nm for these crystals. This means the crystalline (erased) state of the material maintains its opacity not only to visible light but also to ultraviolet and even far ultraviolet light.

The recording film in the crystalline state is naturally opaque to the red laser light ($\lambda = 650$ nm) presently used for DVDs and also to blue-violet laser light ($\lambda = 405$ nm) for Blu-ray discs. If the amorphous (recorded) state holds its transparency to light with shorter wavelengths than blue-violet, even when lasers with a shorter wavelength are developed or light sources emitting half the wavelength of blue-violet are made practical using SHG (second harmonic generation), it is estimated that present amorphous-crystal changes will be able to show sufficient optical difference. In the latter case, the development of a new disc with exactly twice the capacity of a Blu-ray disc, say around 100 GB, is expected.

4.4. Efficiency of GeTe-rich GeTe-Sb₂Te₃ compounds for extremely thin films

As described above, for Blu-ray discs a GeTe-rich GeTe-Sb₂Te₃ compound is employed to obtain sufficient optical changes, even in the form of thin film a few nm thick. This is expected because GeTe compounds have relatively high free electron density. Figure 11 shows composition dependence of unit cell volume (its cube root) at room temperature in GeTe-Sb₂Te₃ pseudobinary compounds (GeTe: Sb₂Te₃ = 10:1, 8:1, 6:1, 4:1, 2:1, and 1:1). As seen in this Figure, $V^{1/3}(\mathbf{x})$ decreases with increased \mathbf{x} , closely resembling a quadric curve. On the other hand, the number of free electrons (N) in the crystalline unit cell varies with $(40+72\mathbf{x})/(1+2\mathbf{x})$, depending on pseudobinary composition \mathbf{x} because Ge, Sb, and Te atoms provide four, five, and six free (conduction) electrons, respectively. This means that free electron density (N/V) rises with the composition of \mathbf{x} , decreasing in the GeTe-rich direction. It is therefore concluded that, even if the recording film is made extremely thin, when making a comparison between films of the same thickness, GeTe-rich pseudobinary crystalline films will have higher opacity and produce a greater optical change between the amorphous and crystalline phases (see Fig. 10) than GeTe-poor versions.

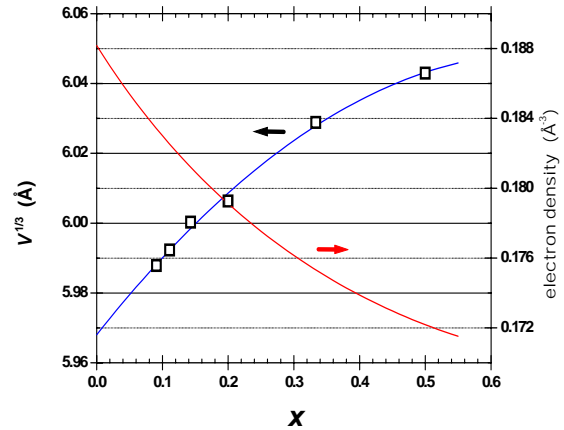


Fig. 11 Pseudobinary composition dependence of cubic square unit cell volume ($V^{1/3}$) shown by squares. The estimated errors are smaller than the marks. The blue curve is a quadratic function fitted using a least-squares method. Composition dependence of the free electron density is indicated by red curve.

5. CONCLUSIONS

Optical recording discs are now in extensive use as rewritable nonvolatile high-density memory storage media, for computers and particularly for home-use videodisc recorders. The most widely used recording material today is GeTe-Sb₂Te₃. We have found that the crystalline phase of this material has, at high temperatures where the phase change from amorphous to crystal is performed, a cubic or pseudo-cubic crystal structure with a spatially isotropic symmetry in which more than one element occupies the lattice sites at random, and the atoms in the crystals thermally oscillate very intensely. These mean that the atomic arrangement of the crystalline phase is close to that of the amorphous, since the atomic arrangement in an amorphous structure is assumed to be spatially isotropic and to have a random atomic arrangement. This enables a transition from amorphous to crystalline phase with small atomic movements: rapidly, in other words¹⁵.

GeTe-rich GeTe-Sb₂Te₃ pseudobinary compounds are adopted for the recording layer of Blu-ray discs, which can record a high volume of information, up to 50 GB. In these compounds, the outermost s and p

orbitals of the three kinds of elements are responsible for bonding with adjacent atoms to form a conduction band in the crystalline state. An enormous number of free (conduction) electrons are present in the microcrystallites of the film, which makes it opaque to light at visible and near-visible wavelengths. The density of free electrons rises with increased GeTe content, emphasizing the difference in optical properties between the amorphous and crystalline phases. This enables sufficient optical changes even in very thin films only a few nanometers thick used for Blu-ray discs.

ACKNOWLEDGMENTS

The synchrotron radiation experiments were performed on BL02B2 at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2003B0478-ND1-np).

We express our sincere thanks to Mr. K. Kato at the JASRI; to Dr. Y. Kubota at the Department of Environmental Sciences, Faculty of Science, Osaka Women's University; and Dr. E. Nishibori, Assistant Professor M. Takata, and Professor M. Sakata at the Department of Applied Physics at Nagoya University for their kind advice on the experiments and analysis.

REFERENCES

1. N. Yamada and T. Matsunaga: *J. Appl. Phys.* **88** (12), 15, 7020-7028 (2000).
2. T. Matsunaga and N. Yamada: *Jpn. J. Appl. Phys.* **41**, 1674-1678 (2002).
3. T. Matsunaga and N. Yamada: *Phys. Rev. B* **69**, 10, 104111 1–8 (2004).
4. T. Matsunaga, N. Yamada and Y. Kubota: *Acta Crystallogr. B* [under submission].
5. E. Nishibori, M. Takata, K. Kato, M. Sakata, Y. Kubota, S. Aoyagi, Y. Kuroiwa, M. Yamakata and N. Ikeda: *Nucl. Instrum. Methods A* **467-468**, 1045–1048 (2001).
6. H. M. Rietveld: *J. Appl. Cryst.* **2**, 65–71 (1969).
7. F. Izumi and T. Ikeda: *Mater. Sci. Forum.* **321-324**, 198-203 (2000).
8. A. J. C. Wilson: *X-Ray Optics* (Methuen, London, 1949).
9. Edited by T. Hahn: *International Tables for Crystallography* (Kluwer, Dordrecht, 1995) Vol. A.
10. J. Goldak, C. S. Barrett, D. Innes, and W. Youdelis: *J. Chem. Phys.* **44**, 3323-3325 (1966)
11. M. Sakata and M. Takata: *Nihon-Kesshōgaku-kaishi* **34**, 100-109 (1992) [in Japanese].
12. S. Kumazawa, Y. Kubota, M. Takata, M. Sakata, and Y. Ishibashi: *J. Appl. Crystallogr.* **26**, 3 453-457 (1993)
13. H. Adachi, M. Tsukada, and C. Satoko: *J. Phys. Soc. Jpn.* **45** 875-883 (1978).
14. N. Yamada and T. Matsunaga: *MRS Fall Meeting Technical Program* (Boston, 2003).
15. T. Matsunaga and N. Yamada: *Jpn. J. Appl. Phys.* [accepted for publication].

Dr. Toshiyuki Matsunaga received his Ph.D. in physics for his work on crystal structures, phase transitions, and bonding natures in intermetallic compounds. Since joining 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.