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Structural investigation of $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ intermetallic compounds in the chalcogenide homologous series

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The crystal structures of $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ were scrutinized using an X-ray powder diffraction method, which revealed that these compounds crystallize in trigonally distorted cubic close-packed structures with a 51-layer period ($R\bar{3}m$). Each layer consists of a triangular atomic net; Te atoms occupy their own specific layers, whereas Ge, Sb and Bi atoms are located in the other layers. In these pseudobinary compounds, random atomic occupations of Ge and Sb/Bi are observed and the layers form two kinds of elemental structural blocks by their successive stacking along the *c* axis. These compounds can be presumed to be isostructural. It is known that the chemical formula of the chalcogenide compounds with the homologous structures found in these pseudobinary systems can be written as $(GeTe)_n(Sb_2Te_3)_m$ or $(GeTe)_n(Bi_2Te_3)_m$ (n, m: integer); the $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ investigated in this study, which correspond to the case in which $n = 1$ and $m = 3$, naturally have $3 \times l = 51$-layer structures according to a formation rule $l = 2n + 5m$ commonly found in the compounds of these chalcogenide systems (l represents the number of layers in the basic structural unit). Calculations based on the density functional theory revealed that these materials are compound semiconductors with very narrow band gaps.

1. Introduction

It has been found that in thermal equilibrium, the GeTe–Sb_2Te_3 or GeTe–Bi_2Te_3 pseudobinary system forms various intermetallic compounds represented by the chemical formula $(GeTe)_n(Sb_2Te_3)_m$ or $(GeTe)_n(Bi_2Te_3)_m$ (n, m: integer); these compounds exist in homologous phases (Shelimova *et al.*, 2000). These chalcogenide compounds, which can be described as trigonal structures with cubic close-packed atomic layers, are of considerable importance, because the alloys of these systems are used for manufacturing rewritable optical recording materials as well as for future non-volatile electronic memories and thermoelectric energy conversion devices. As a result, many structural investigations have already been carried out on the compounds of these systems. With regard to the GeTe–Sb_2Te_3 system, it has been found that a series of intermetallic compounds crystallized in homologous structures are present from GeTe:Sb_2Te_3 = 9:1 through to 1:3 (Shelimova *et al.*, 2000). The GeTe–Bi_2Te_3 system also has a series of homologous structures (Shelimova *et al.*, 1997). Among these intermetallic compounds, $Ge_3Sb_2Te_6$ (Matsunaga *et al.*, 2007*a*), $Ge_2Sb_2Te_5$ (Matsunaga *et al.*, 2004), $Ge_2Bi_2Te_5$ (Matsunaga *et al.*, 2007*b*), $GeSb_2Te_4$ (Karpinsky *et al.*, 1998*a*; Matsunaga & Yamada, 2004), $GeBi_2Te_4$ (Karpinsky *et al.*, 1998*b*) and $GeSb_4Te_7$ (Matsunaga *et al.*, 2008) have already been scrutinized by single-crystal or powder X-ray

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Table 1
Experimental details.

For all structures: trigonal, $R\bar{3}m$, $Z = 3$. Experiments were carried out at 92 K using a BL02B2 diffractometer. Refinement was on 39 parameters.

	(I)	(II)
Crystal data		
Chemical formula	$GeSb_6Te_{10}$	Bi_6GeTe_{10}
M_r	2079.1	2602.5
a, c (Å)	4.236, 101.5087	4.3515, 101.8739
V (Å^3)	1577.38	1670.57
Radiation type	Synchrotron, $\lambda = 0.42354$ Å	Synchrotron, $\lambda = 0.42308$ Å
Specimen shape, size (mm)	Cylinder, 0.3 mm diameter	Cylinder, 0.2 mm diameter
Data collection		
Specimen mounting	Sealed quartz capillary tube	Sealed quartz capillary tube
Data collection mode	Transmission	Transmission
Scan method	Fixed	Fixed
2θ values (°)	$2\theta_{min} = 1.20$, $2\theta_{max} = 56.00$, $2\theta_{step} = 0.01$	$2\theta_{min} = 1.10$, $2\theta_{max} = 54.00$, $2\theta_{step} = 0.01$
Refinement		
R factors and goodness of fit	$R_p = 0.041$, $R_{wp} = 0.057$, $R_{exp} = 0.012$, $R(F) = 0.040$, $\chi^2 = 22.6$	$R_p = 0.027$, $R_{wp} = 0.038$, $R_{exp} = 0.010$, $R(F) = 0.055$, $\chi^2 = 14.4$
No. of data points	5481	5291
No. of restraints	19	19
$\Delta\sigma_{max}$	13.972	8.549

diffraction. However, the detailed crystal structures of many other compounds in this series have not yet been clarified, because they have very complicated long-period structures and their single crystals are rather difficult to isolate. In the present study, however, we succeeded in determining the crystal structures of $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ by using a synchrotron powder diffraction method, which revealed that these two pseudobinary compounds have 51-layered homologous structures with the space group $R\bar{3}m$ as Shelimova *et al.* (2000) had expected. These structures are characterized by stacking of NaCl-type blocks along the c axes with very long cell dimensions. Calculations based on density functional theory (DFT) demonstrate that these materials are compound semiconductors with very narrow band gaps.

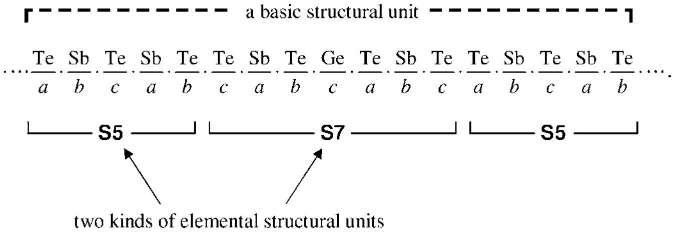
2. Experimental

We prepared $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ by melting a stoichiometric mixture of 99.999% pure Ge, Sb, Bi and Te in an argon atmosphere and then quenching it in ice water. The resulting alloy ingots were respectively annealed at 773 K for 32 d, at 453 K for 9 d + at 803 K for 5 d in an argon atmosphere. The powder specimens produced by crushing the complete ingots were packed into quartz capillary tubes with internal diameters of 0.3 mm for $GeSb_6Te_{10}$ and 0.2 mm for $GeBi_6Te_{10}$. To insulate the specimens from the atmosphere, we sealed the openings of the capillaries using an oxyacetylene flame.

We performed diffraction experiments at 92 K using the BL02B2 beamline at the Japan Synchrotron Radiation Research Institute (Nishibori *et al.*, 2001). The energy of the incident beam was approximately 29.4 keV. Intensity data were collected using a Debye–Scherrer camera with a 287 mm radius. An imaging plate with a pixel area of 100 μm^2 was used as the detector. The angular resolution was 0.02°. The crystal structures were examined and refined using the Rietveld method (Rietveld, 1969).[1] The programs *RIETAN*2000 (Izumi & Ikeda, 2000) and *JANA*2000 (Petříček & Dušek, 2000) were used for this purpose; intensity data in increments 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 Å) powder as a reference specimen at room temperature under the same conditions. Neutral atomic scattering factors were used for the structural analysis, and one isotropic displacement parameter was used for all the Te atoms while a second was applied to the other two atoms. Experimental details are given in Table 1.

3. Results and discussion

The structure of compound $GeSb_6Te_{10}$ ($GeBi_6Te_{10}$) is assumed to have the stacking (Shelimova *et al.*, 2000) shown in (I).



(I)

The structure of $GeBi_6Te_{10}$ can be obtained by replacing Sb with Bi. This layer stacking, which shows a basic structural unit along the c axis in a unit cell, comprises two kinds of NaCl-type blocks (slabs), **S5** and **S7**, as elemental structural units; a unit cell consists of three stacks of the basic structural units formed by **S5** + **S7** + **S5** (see Fig. 1). The neighboring basic units along the c axis are obtained by shifting a unit in the $[\bar{1}10]$ direction by 1/3 or −1/3. The layer sequence in (I) and Fig. 1 for these two crystals exhibits an ideal perfectly ordered structural model. However, as mentioned in §1, several compounds in the pseudobinary $GeTe–Sb_2Te_3$ or $GeTe–Bi_2Te_3$ system have been precisely examined using X-ray diffraction methods, which revealed that in all these structures Te atoms

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SO5032). Services for accessing these data are described at the back of the journal.

occupied their specific layers, whereas the Ge and Sb (Bi) atoms were located in the remaining layers with partial atomic disordering. We then assumed that the Ge and Sb layers are randomly occupied by their atoms in the $GeSb_6Te_{10}$ crystal and carried out Rietveld analysis to determine the distribution of the Ge and Sb atoms together with other structural parameters under the condition that these two atoms retain their stoichiometry. In addition, we also analyzed the structure of $GeBi_6Te_{10}$ in the same manner as that of $GeSb_6Te_{10}$. These analyses revealed that $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ have almost the same structures, which consist of Te layers and Ge/Sb (Ge/Bi) mixed layers. The final results of the structural analyses are listed in Table 2 and shown in Fig. 2; these results show very low R factors. The crystal structure of $GeSb_6Te_{10}$ ($GeBi_6Te_{10}$) is shown in Fig. 1. The $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ crystals, as shown in this figure, have 51-layer structures (17*R*), in which Ge and Sb (Bi) atoms are actually scattered over and across their specific sites; however, the ratio of the two atoms differs among sites. As listed in Table 2, the 1:3*a* site tends to be preferred by Ge atoms; on the other hand, the 5:6*c*, 6:6*c* and 9:6*c* sites are preferentially occupied by Sb (Bi) atoms. If the respective sites were only occupied by the preferred atoms, the layer stacking of this hypothetical, perfectly ordered structure would be expressed by model (I).

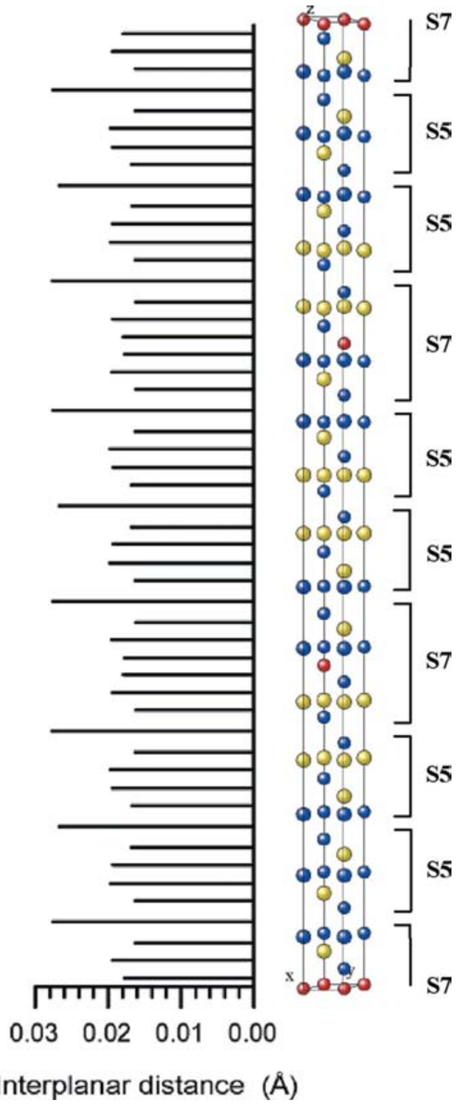

Figure 1
Atomic arrangement of $GeSb_6Te_{10}$ ($GeBi_6Te_{10}$) in the perfectly ordered structural model [refer to the stacking sequence (I)], in which red, yellow and blue spheres represent Ge, Sb(Bi) and Te atoms. The interplanar distances in the unit cell are shown in the graph beside the structural model. This trigonal structure consists of sequential stacking of basic structural units (**S5** + **S7** + **S5**) formed by the elemental blocks **S** separated by wider interplanar gaps.

Table 2
Structural parameters for $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ at 92 K obtained by Rietveld analyses.

Of the eight kinds of g parameters at the Ge/Sb (Ge/Bi) sites in the pseudobinary compounds, $g_{Ge}^{5:6c}$ and $g_{Ge}^{6:6c}$ were set as independent variables in these analyses to estimate the occupation rates of Ge and Sb (Ge and Bi) atoms at their four sites. Two overall isotropic displacement parameters were separately applied to the four Ge/Sb (Ge/Bi) sites and to the five Te sites. The diffraction data used for the analysis: $1.20 \leq 2\theta \leq 56.00^\circ$. The x and y coordinates are all zero in this asymmetric unit chosen to describe the structure.

	Site	Occ.	x	y	z	B (Å^2)
Ge/Sb1	1:3*a*	0.50 (3)/0.50	0	0	0	1.50 (3)
Te2	2:6*c*	1.0	0	0	0.05337 (4)	0.44 (2)
Te3	3:6*c*	1.0	0	0	0.11698 (6)	0.44
Te4	4:6*c*	1.0	0	0	0.17986 (4)	0.44
Ge/Sb5	5:6*c*	0.02 (2)/0.98	0	0	0.23559 (6)	1.50
Ge/Sb6	6:6*c*	0.18 (2)/0.82	0	0	0.29560 (5)	1.50
Te7	7:6*c*	1.0	0	0	0.35090 (5)	0.44
Te8	8:6*c*	1.0	0	0	0.41426 (5)	0.44
Ge/Sb9	9:6*c*	0.05/0.95	0	0	0.46956 (6)	1.50

$GeBi_6Te_{10}$: $R_{wp} = 0.038$, $R_p = 0.027$, $RF_{obs} = 0.055$, R_{wp} expected = 0.010, $a = 4.3514$ (1) and $c = 101.874$ (5) Å. The diffraction data used for the analysis: $1.10 \leq 2\theta \leq 54.00^\circ$.

	Site	Occ.	x	y	z	B (Å^2)
Ge/Bi1	1:3*a*	0.46 (2)/0.54	0	0	0	0.91 (3)
Te2	2:6*c*	1.0	0	0	0.05496 (7)	1.14 (5)
Te3	3:6*c*	1.0	0	0	0.11734 (10)	1.14
Te4	4:6*c*	1.0	0	0	0.17881 (7)	1.14
Ge/Bi5	5:6*c*	0.06 (1)/0.94	0	0	0.23664 (4)	0.91
Ge/Bi6	6:6*c*	0.18 (1)/0.82	0	0	0.29551 (4)	0.91
Te7	7:6*c*	1.0	0	0	0.35089 (9)	1.14
Te8	8:6*c*	1.0	0	0	0.41407 (9)	1.14
Ge/Bi9	9:6*c*	0.03/0.97	0	0	0.46986 (4)	0.91

Interatomic distances obtained for the $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ structures are listed in Table 3. Each atom at the nine sites is coordinated by six atoms. However, except for the Ge/Sb1 atom (Ge/Bi1 atom) at the $3(a){:}\bar{3}m$ site, the other eight atoms located at the $6(c){:}3m$ sites have $3 + 3$ neighbors at varying distances; these neighbors are scattered from 2.916 to 3.627 Å for $GeSb_6Te_{10}$ and from 3.060 to 3.526 Å for $GeBi_6Te_{10}$. As can be observed from Table 3, the Te—Te distances between the two neighboring NaCl-type blocks are markedly longer than the others, which make the interplanar distances between Te–Te layers longer than those of the other layers; these interplanar distances are also longer than those in the other pseudobinary homologous compounds described in §1. In Fig. 1 all interplanar distances in a unit cell are graphed beside the structural model; it can be observed from this figure that all consecutive NaCl-type blocks are separated from each other by these wide Te–Te interplanar gaps. These Te–Te layers are assumed to be connected by the van der Waals-type weak forces as they are in the other homologous compounds (Karpinsky *et al.*, 1998*a*; Matsunaga *et al.*, 2008).

To examine the electronic structures of these materials, we performed band calculations based on DFT. The program used for the DFT calculations was *CHASE*-3*PT* (Advancesoft Co. Ltd, 2002); the calculations were performed using pseudopotentials with electronic configurations of Ge $4s^24p^2$, Sb $5s^25p^3$, Bi $6s^26p^3$ and Te $5s^25p^4$ in the generalized gradient approximation of the plane-wave method. *K* points in a reciprocal rhombohedral unit cell were divided into 4 × 4 × 4 points; the tetrahedron method was used for the total energy calculations. For our analyzed $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$, the perfectly ordered structural models were used to simplify the calculations; the structural parameters used for the calculations are listed in Table 2. The density of states (DOS) obtained for the valence electrons (Fig. 3) revealed that very narrow band gaps are present between the valence and conduction bands, suggesting that these compounds are semiconducting materials. Shelimova *et al.* (2001) experimentally observed that the series of $(GeTe)_n(Sb_2Te_3)_m$ and $(GeTe)_n$-$(Bi_2Te_3)_m$ homologous compounds including $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ are degenerate semiconductors. Assuming that no defects exist both in the crystal and in the structure, it can be said that these two compounds with 51-layer homologous structures are compound semiconductors with very narrow band gaps. We have confirmed that other $(GeTe)_n(Sb_2Te_3)_m$ homologous compounds, $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, $Ge_1Sb_2Te_4$ and $GeSb_4Te_7$ (and $Ge_2Bi_2Te_5$, Matsunaga *et al.*, 2007*b*, in the GeTe–Bi_2Te_3 pseudobinary system) are also all semiconducting materials through the calculations performed in the same manner (Matsunaga, Kojima & Yamada, 2007).

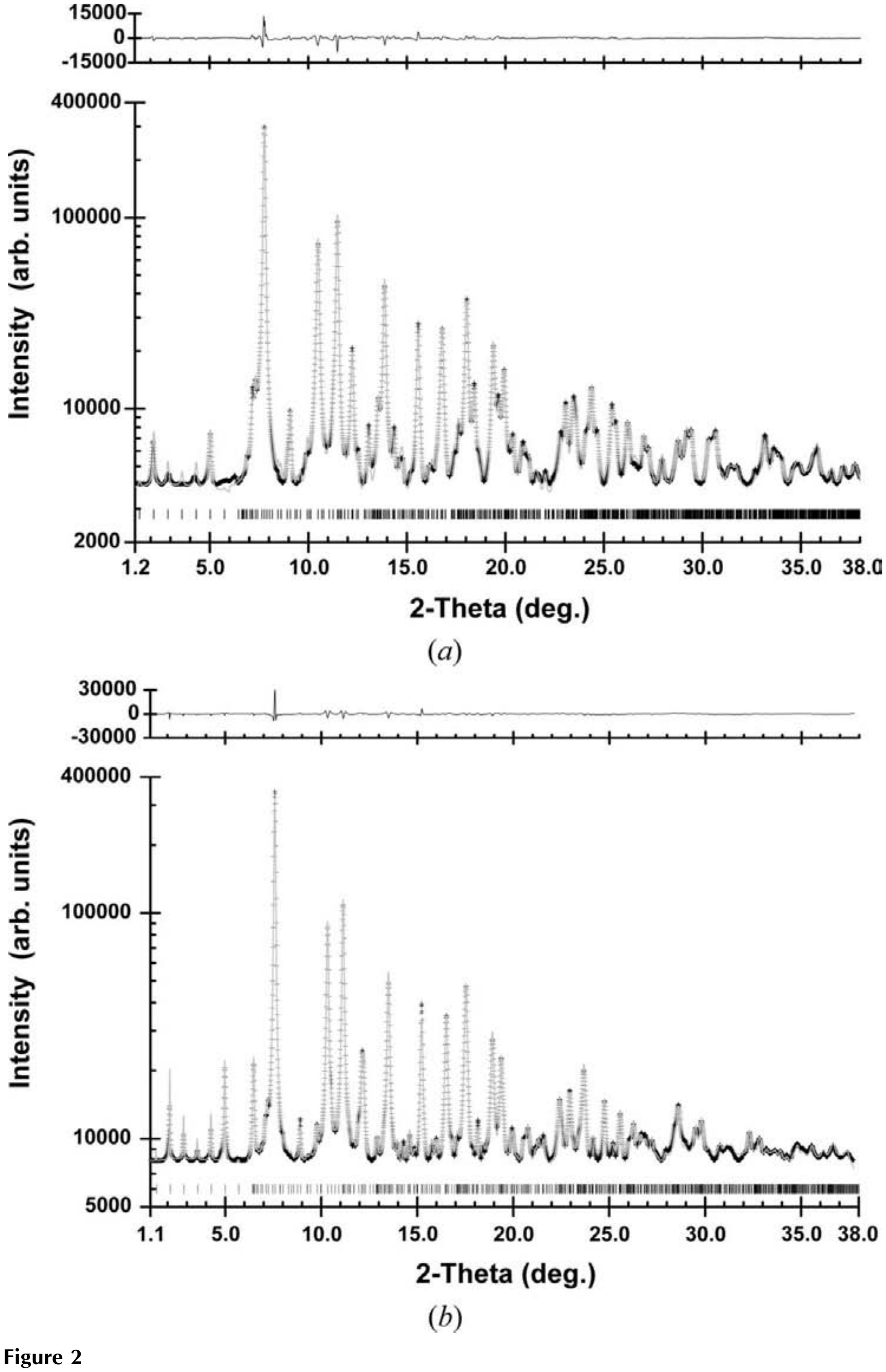

Figure 2
Observed (+) and calculated (gray line) X-ray diffraction profiles of (*a*) $GeSb_6Te_{10}$ and (*b*) $GeBi_6Te_{10}$ at 92 K. A difference curve (observed–calculated) appears at the top of each figure; reflection markers are indicated by vertical spikes below the diffraction patterns.

4. Conclusions

The $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ crystals have 51-layered cubic close-packed stacking structures in common ($R\bar{3}m$) according to a very probable rule that chalcogenides compounds $(IV_1VI_1)_n(V_2VI_3)_m$ form *P*: $(2n + 5m)$-layer and *R*: $3 \times (2n + 5m)$-layer structures. In the two pseudobinary structures,

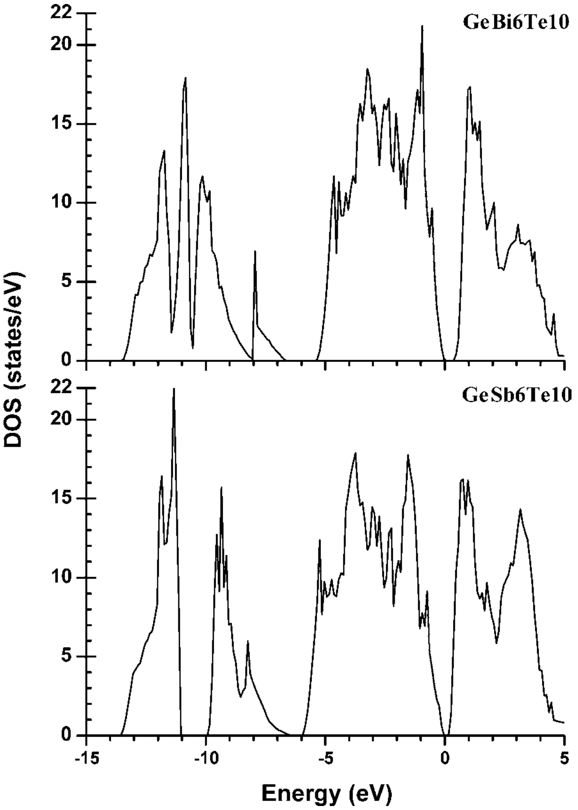

Figure 3
DOS diagrams for $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ obtained using band calculations. The structural parameters used for the calculations are listed in Table 2. The Fermi level corresponds to 0 eV. Narrow band gaps can be observed between the valence and conduction bands at the Fermi level, which implies that these materials are semiconductors.

Table 3
Interatomic distances (Å) for $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$.

The atomic pairs for $GeSb_6Te_{10}$ and $GeBi_6Te_{10}$ are represented by their perfectly ordered structural models.

$GeSb_6Te_{10}$		$GeBi_6Te_{10}$	
Ge1—Te7 ×6	3.027 (3)	Ge1—Te7 ×6	3.084 (5)
Te2—Sb6 ×3	2.916 (4)	Te2—Bi6 ×3	3.060 (5)
Te2—Te8 ×3	3.716 (5)	Te2—Te8 ×3	3.634 (8)
Te3—Sb9 ×3	3.129 (5)	Te3—Bi9 ×3	3.183 (7)
Te3—Sb5 ×3	3.130 (5)	Te3—Bi5 ×3	3.277 (7)
Te4—Sb9 ×3	3.008 (4)	Te4—Bi9 ×3	3.110 (5)
Te4—Te4 ×3	3.627 (4)	Te4—Te4 ×3	3.526 (7)
Sb5—Te8 ×3	2.982 (4)	Bi5—Te8 ×3	2.992 (5)
Sb5—Te3 ×3	3.130 (5)	Bi5—Te3 ×3	3.277 (7)
Sb6—Te2 ×3	2.916 (4)	Bi6—Te2 ×3	3.060 (5)
Sb6—Te7 ×3	3.189 (5)	Bi6—Te7 ×3	3.251 (6)
Te7—Ge1 ×3	3.027 (3)	Te7—Ge1 ×3	3.084 (5)
Te7—Sb6 ×3	3.189 (5)	Te7—Bi6 ×3	3.251 (6)
Te8—Sb5 ×3	2.982 (4)	Te8—Bi5 ×3	2.992 (5)
Te8—Te2 ×3	3.716 (5)	Te8—Te2 ×3	3.634 (8)
Sb9—Te4 ×3	3.008 (4)	Bi9—Te4 ×3	3.110 (5)
Sb9—Te3 ×3	3.129 (5)	Bi9—Te3 ×3	3.183 (7)

the Ge/Sb (Ge/Bi) and Te layers are stacked alternately; Te atoms exclusively occupy their own specific layers, whereas Ge and Sb (Bi) atoms are randomly located at the other layers, causing a partially disordered atomic occupation in these layers. Assuming that no defects exist in the crystal and structure, these compounds can be considered as compound semiconductors with a very narrow band gap.

The synchrotron radiation experiments were performed on BL02B2 at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI). We express our sincere gratitude to Drs K. Kato and K. Osaka at JASRI and to graduate students N. Yasukawa, A. Yoshimura and T. Murata of the Graduate School of Science at Osaka Prefecture University for their assistance with the experiments. The structural model in Fig. 1 was displayed using the Java Structure Viewer (JSV 1.08 lite) created by Dr Steffen Weber.

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