Overview of the GeTe-Sb$_2$Te$_3$ pseudobinary crystalline phase

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Today, GeTe-Sb$_2$Te$_3$ pseudobinary compounds are in wide use as the active materials in rewritable phase-change optical disks and non-volatile electronic memories. This pseudobinary system has two kinds of crystalline phase: a metastable phase with NaCl-type structures and a stable homologous phase with trigonal structures that have cubic close-packed long-period periodicity. The structures of these two phases resemble each other in that Te and Ge/Sb layers are stacked alternately. Both have octahedrally coordinated structures and the characteristics of semiconducting materials.
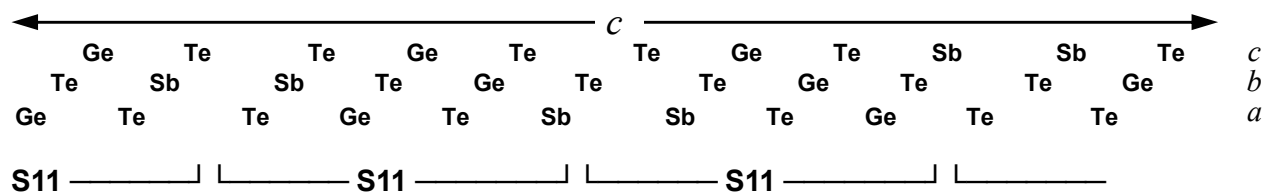
One of the most widely used memory materials for rewritable phase change optical disks such as DVD-RAMs (digital versatile disk - random access memory) or Blu-ray discs is GeTe-Sb$_2$Te$_3$ pseudobinary compound. These chalcogenide materials are of considerable importance, since alloys in this system are used as rewritable optical recording materials as well as for non-volatile electronic memories and thermoelectric energy conversion devices; for this reason, many investigations have been conducted on this system's compounds. The pseudobinary system has two kinds of crystalline phases: one is a metastable phase with NaCl-type structures that contains an enormous number of intrinsic vacancies, and the other is a stable homologous phase with a series of intermetallic compounds which can be described as trigonal structures with cubic close-packed long-period periodicity. The structures of these two phases, however, are similar to each other: they fundamentally consist of alternately stacked Te and Ge/Sb layers. Another common feature is that Ge and Sb are randomly arranged within the Ge/Sb layer. The major structural differences are only whether Te-Te consecutive layers exist in the stacks and whether the Ge/Sb layers contain vacancies. We will show the structural characteristics of the metastable phase first.

In the case of GeTe(1-x)-Sb$_2$Te$_3$(x) pseudo-binary compounds (from $x = 0$ to at least 2/3), all their amorphous films can be crystallized into simple NaCl-type structures, irrespective of their composition, through instantaneous laser irradiation. At room temperature, GeTe and several compounds with GeTe-rich compositions crystallize not into the cubic phase but into the rhombohedral phase (space group: $R3m$) with an NaCl-type structure slightly deformed along one of the three-fold rotation axes (Fig. 1). These structures, however, can basically be regarded as being of the cubic NaCl type. We have previously reported our
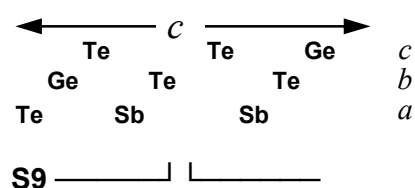
structural analysis results for these NaCl-type metastable phases [1], [2], [3]. These cubic structures belong to the $Fm\bar{3}m$ space group. Te occupies 100% of the 4(a) sites, while Ge, Sb, and vacancies are randomly located at the 4(b) sites, regardless of the compound's composition. In each of these structures, which can be regarded as a six-layer homologous structure in hexagonal notation, every atom is coordinated by six neighboring atoms, forming an octahedron. Each atom is connected with its adjacent six atoms through orthogonal p-p covalent bondings. The bonding electrons occupy only the valence band, which is chiefly formed by the bonding molecular orbitals in the periodicity of the crystal lattice, resulting in a stable structure. An Sb atom, which is a Group V element, has three p electrons, meaning that it has one excess p electron compared with Ge (a Group IV element). When GeTe is replaced by Sb_2Te_3, therefore, a vacancy is generated at the rate of two substituted Sb atoms to retain the closed shell structure of the p orbitals, as in the case of GeTe. These metastable compounds, including GeTe, are all compound semiconductors in which outermost electrons occupy only the valence band, provided no defects are present in the crystal except for the above intrinsic vacancies [4]. According to the mechanism of vacancy creation, the fraction of these vacancies in the Na sites $v(x)$ is expected to change continuously in proportion to $x/(1 + 2x)$; as demonstrated in Fig. 2, this composition dependence of the vacancy fraction has been experimentally confirmed. This Figure shows that an enormous number of vacancies are present in the crystal, especially in Sb_2Te_3-rich compositions. The numerous vacancies are likely to relieve the volume expansion accompanied by the increase in Sb_2Te_3; in fact, the cubic root unit cell volume $V^{1/3}(x)$ has a strong correlation with the vacancy rate $v(x)$, as seen in the same Figure [4]. These vacancies will also cause a very large disordering of the atomic arrangement. It has been pointed out that disorder of this type is caused in the metastable $Ge_2Sb_2Te_5$ crystal [5, 6]. We reexamined the atomic arrangement in this metastable crystal by PDF (Pair Distribution Function) [7] analysis using the x-ray diffraction data. The results obtained are shown in Table I and Figure 3. As shown in this Table, large atomic displacements of Ge and Sb were detected also in our analysis. This result shows, of course, no more than one of many possible disordered atomic arrangements, although, the shift vectors from their equilibrium positions are almost randomly oriented; in other words, this static disorder has little preferred orientation. This has been also confirmed by our RMC (Reverse Monte Carlo) analysis [8]. The vacancies are randomly distributed in the crystals; for the diffraction patterns from these metastable crystals exhibit no additional peak, showing that the symmetry declines owing to ordering of the vacancies. Every atomic arrangement in these metastable crystals therefore holds a cubic or rhombohedral lattice symmetry, retaining its lattice periodicity. Next, we will show the structural characteristics of the stable phase.

It is known that in a thermally equilibrated state, the GeTe-Sb_2Te_3 pseudobinary system forms various intermetallic compounds represented by the chemical formula $(GeTe)_n(Sb_2Te_3)_m$ [9]. These compounds, which are known as a homologous series, can be described as structures with cubic close-packed periodicity ($\cdots abcabc\cdots$), where the stacking rules of the Ge, Sb, and Te layers differ from each other. In these compounds, $Ge_3Sb_2Te_6$ [10], $Ge_2Sb_2Te_5$ [2], $Ge_1Sb_2Te_4$ [1], [9], $Ge_1Sb_4Te_7$ [11] and Sb_2Te_3 [12] have already been analyzed in detail by X-ray diffraction. Every structure of these stable compounds can be understood as a cubic closed packed structure of the basic structural unit, an NaCl slab (**S**), as shown below and in Fig. 4.
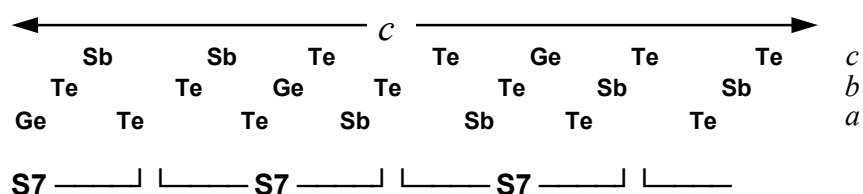
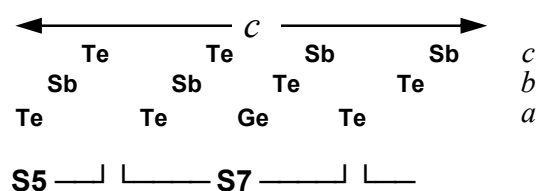(a) $Ge_3Sb_2Te_6$ [$n = 3$, $m = 1$ ($x = 1/4$); $33R$ ($R\bar{3}m$), $a = 4.1978\,(1)$, $c = 62.021(2)$ Å (90K)]

```
    ◄──────────────────────────── c ────────────────────────────►
      Ge      Te      Te      Ge      Te      Te      Ge      Te      Sb      Sb      Te      c
   Te      Sb      Sb      Te      Ge      Te      Te      Ge      Te      Te      Ge          b
Ge      Te      Te      Ge      Te      Sb      Sb      Te      Ge      Te      Te              a

S11 ──────┘ └────── S11 ──────┘ └────── S11 ──────┘ └──────
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(b) $Ge_2Sb_2Te_5$ [$n = 2$, $m = 1$ ($x = 1/3$); $9P$ ($P\bar{3}m1$), $a = 4.2247\,(1)$, $c = 17.2391(4)$ Å (RT)]

```
    ◄──── c ────►
      Te      Te      Ge      c
   Ge      Te      Te          b
Te      Sb      Sb              a

S9 ──────┘ └──────
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(c) $Ge_1Sb_2Te_4$ [$n = 1$, $m = 1$ ($x = 1/2$); $21R$ ($R\bar{3}m$), $a = 4.2251(1)$, $c = 40.995(2)$ Å (90K)]

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    ◄────────────── c ──────────────►
      Sb      Sb      Te      Te      Ge      Te      Te      c
   Te      Te      Ge      Te      Te      Sb      Sb          b
Ge      Te      Te      Sb      Sb      Te      Te              a

S7 ────┘ └──── S7 ────┘ └──── S7 ────┘ └──────
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(d) $Ge_1Sb_4Te_7$ [$n = 1$, $m = 2$ ($x = 2/3$); $12P$ ($P\bar{3}m1$), $a = 4.2360\,(3)$, $c = 23.761\,(2)$ Å (90K)]

```
    ◄────────── c ──────────►
      Te      Te      Sb      Sb      c
   Sb      Sb      Te      Te          b
Te      Te      Ge      Te              a

S5 ──┘ └────── S7 ────┘ └──
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(e) Sb_2Te_3 [$n = 0$, $m = 1$ ($x = 1$); $5R$ ($R\bar{3}m$), $a = 4.2512\,(1)$, $c = 30.3177(3)$ Å (90K)]

```
    ◄────────── c ──────────►
      Te      Te      Te      Sb      Sb      c
   Sb      Sb      Te      Te      Te          b
Te      Te      Sb      Sb      Te              a

S5 ──┘ └────── S5 ────┘ └──── S5 ──┘ └──
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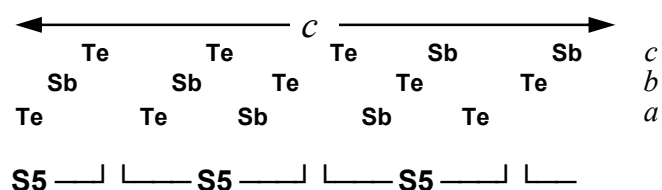
(1)

These are the perfectly ordered structural models. Each NaCl slab also consists of alternating stacks of Te and Ge/Sb layers, and both ends of the slab are covered with Te layers without exception, except for GeTe. GeTe ($n = 1$, $m = 0$) is an NaCl-type structure in which a six-layered structure with alternate stacks of Te and Ge/Sb layers repeats infinitely along the c-axis ($\mathbf{S}\infty$). In all of these compounds, every atom is

coordinated by six atoms. However, except for the atoms at the center layer of the slabs, the other atoms have 3 + 3 neighbors at shorter and longer distances, which scatters interatomic distances from 2.9 to 3.8 Å. Those for Ge-Te and Sb-Te pairs are in the range of 2.9~ 3.2 Å, whereas the Te–Te distance (about 3.6 ~ 3.8 Å) between the neighboring two NaCl slabs is markedly longer than the others, which makes the interplanar distance between Te–Te layers longer than any of the others. These consecutive Te layers, namely the neighboring two NaCl slabs, are assumed to be connected by a weak interaction such as van der Waals bonding; on the other hand, the atoms within the slabs are considered to be strongly connected with adjacent atoms by covalent bonding [13]. It is known that, when heating metastable NaCl structures, they transform into corresponding homologous structures showing exothermic peaks in their DSC (Differential Scanning Calorimetry) curves [14], meaning that homologous structures are, as a matter of course, more stable than the corresponding metastable ones. This suggests that the atoms inside the NaCl slabs are connected by more stable covalent bonds than those in the metastable crystal, which is demonstrated by the reduction of the mean volume per single atom shown in Fig. 2(b). Another feature of the atomic configuration of these stable compounds is that the Te atoms fully occupy their specific sites, unlike the Ge and Sb atoms, which are scattered across their sites in the same way as in a metastable structure. The ratio of Ge and Sb, however, differs between sites and compounds; generally, Ge atoms prefer to be located around the centers of the NaCl slabs, whereas Te atoms congregate near the Te-Te consecutive layers (see Fig. 4). If the Ge and Sb atoms individually occupy their preferred sites according to an atomic distribution pattern that satisfies their stoichiometric compositions, the structures of these materials can be approximated by the perfectly ordered ones shown in the stacking sequences (1). Figure 5 shows some of the densities of state (DOS) obtained by band calculations using these perfectly ordered structural models. The DOS diagrams for these materials show that (narrow) band gaps are present between the valence and conduction bands, as expected. Shelimova *et al*. [15] experimentally observed that a series of $(GeTe)_n(Sb_2Te_3)_m$ homologous compounds are degenerated *p*-type semiconductors, strongly suggesting that these compounds are all, provided they have no defects in their crystals, semiconducting materials as well as being in a metastable phase. Shelimova and her colleagues have also found, in their laborious work on several chalcogenide compound systems besides the $GeTe\text{-}Sb_2Te_3$ pseudobinary system, that some other new homologous structures [$Ge_4Sb_2Te_7(39R)$, $Ge_1Sb_6Te_{10}(51R)$, $Ge_1Sb_8Te_{13}(66R)$, etc.,] exist in these systems (for example, see reference [16]). We intend to analyze the precise structures of these compounds and reveal their crystallographic properties.

The NaCl-type structure in the metastable phase crystallizes into a six-layer cubic close-packed structure in which the Ge/Sb layer and Te layers are alternately stacked. The Ge/Sb layer in the metastable phase contains as much as $x/(1 + 2x)$ (for example, 20 at. % vacancies in the metastable $Ge_2Sb_2Te_5$ crystal), which makes the structure very sparse spatially. The mean volume per single atom is, therefore, larger than that in the stable phase [see Fig. 2(b)]. On the other hand, in the stable phase, Te and Ge/Sb are stacked alternately $2n+5m$ times to form an NaCl slab, and then the slabs are stacked to construct a long-period cubic close-packed trigonal structure. Te layers cover both ends of a slab. In addition, the stable phase has no intrinsic vacancies in the Ge/Sb layer, unlike the metastable phase. The structures of the metastable phase and stable phase, however, are similar to each other; basically Te and Ge/Sb are stacked alternately. Both

have regular or distorted octahedral coordination structures and the characteristics of a semiconducting material. Another common feature is that Ge and Sb are randomly arranged to make the Ge/Sb layer. The major structural differences are, as mentioned above, only whether Te-Te consecutive layers are present in the stacking and whether the Ge/Sb layers contain vacancies.

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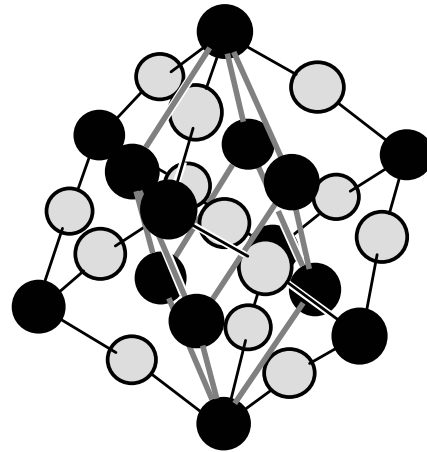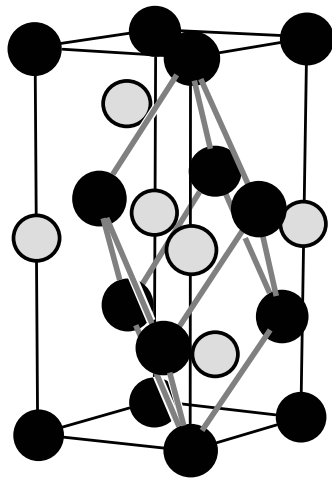
GeTe (RT)

Fig. 1. Structure of the distorted NaCl-type low-temperature phase ($R3m$) shown with both the rhombohedral (gray thick lines) and hexagonal (black thin lines) unit cells in the left-hand Figure. Black circles indicate Te atoms, whereas grey 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, as shown in the right-hand Figure.
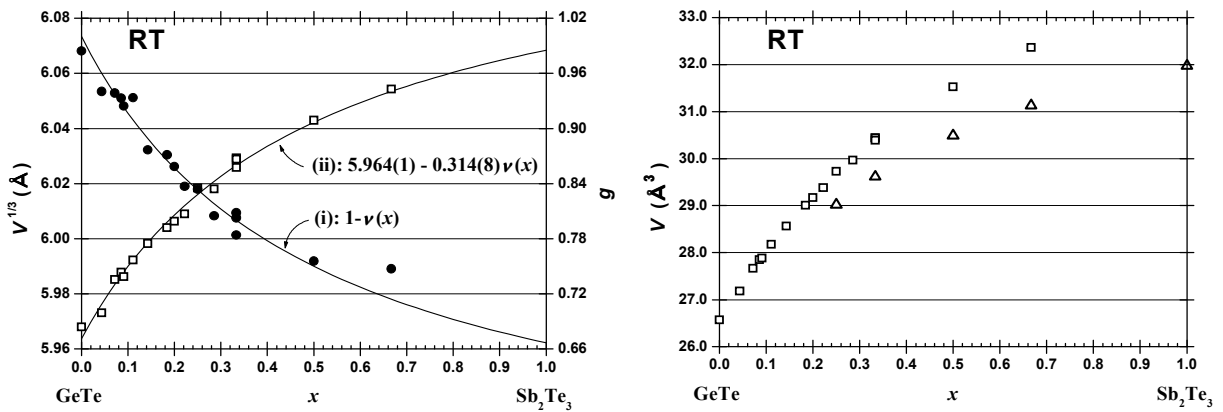

Fig. 2. (a: top) Composition dependence of the g parameter for the NaCl-type metastable compounds, which indicates site occupancy of Ge + Sb atoms at Na sites, shown by black circles, and that of the cubic root *unit cell* volume ($V^{1/3}$) by open squares. The horizontal axis, x, indicates the fraction of Sb_2Te_3 in the GeTe - Sb_2Te_3 pseudo-binary system. The curves in the Figure are (i): $1-v(x)$ and (ii): $a + bv(x)$, which is the least squares fitting result obtained by taking vacancy contribution into account (see Ref. [4]). (b: bottom) Temperature dependence of the mean volume per *single atom*. Squares and triangles show those of the metastable and stable phase, respectively. The data for Sb_2Te_3 was quoted from reference [12].

6

Table I. Refined local crystallographic parameters for 8 sites model [6] of the metastable Ge$_2$Sb$_2$Te$_5$ crystal at 90 K. We assumed a cubic unit cell, which corresponds to that of the NaCl-type structure for this metastable phase, to estimate the disorder of the atomic configuration. The lattice constant was determined to be a=6.00953(1) Å and the final R-factor is 6.1%.

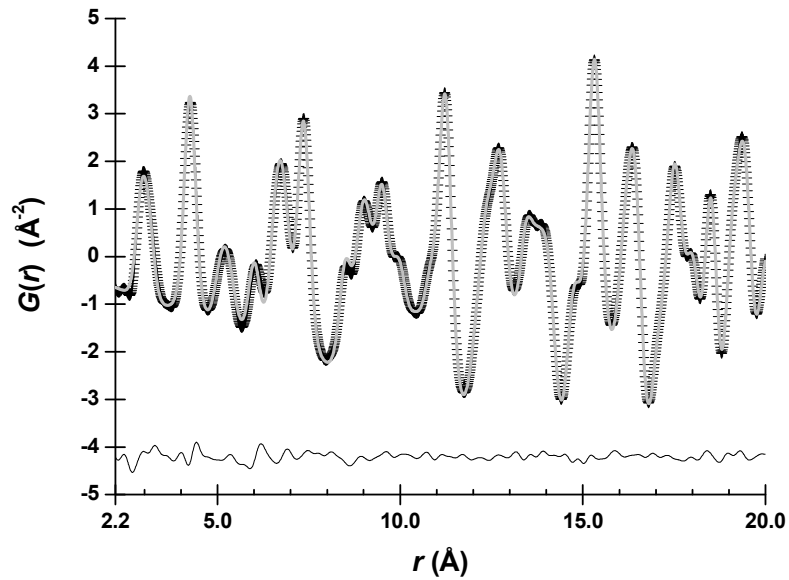|	x	y	z	g	B eq (Å^2)
Ge	0.529(1)	0.515(2)	0.518(2)	0.4	1.56
Ge	0.476(1)	0.026(2)	0.016(2)	0.4	1.56
Ge	0.016(3)	0.460(1)	0.014(4)	0.4	1.56
Ge	0.008(1)	-0.007(1)	0.447(1)	0.4	1.56
Sb	0.476(1)	0.482(1)	0.520(1)	0.4	1.39
Sb	0.530(1)	-0.007(1)	0.007(1)	0.4	1.39
Sb	0.025(2)	0.525(1)	0.019(2)	0.4	1.39
Sb	0.016(1)	-0.014(2)	0.524(1)	0.4	1.39
Te	0	0	0	1	0.99
Te	0	0.503(1)	0.503	1	0.99
Te	0.506(1)	0	0.501(1)	1	0.99
Te	0.509(1)	0.508(1)	0.003(1)	1	0.99

Fig. 3. Observed (+ marks), calculated (thick gray line), and difference (thin line) pair distribution function profiles in the fitted range of 2.2 < r < 20.0 Å. The program PDFgui [7] was used for this analysis.
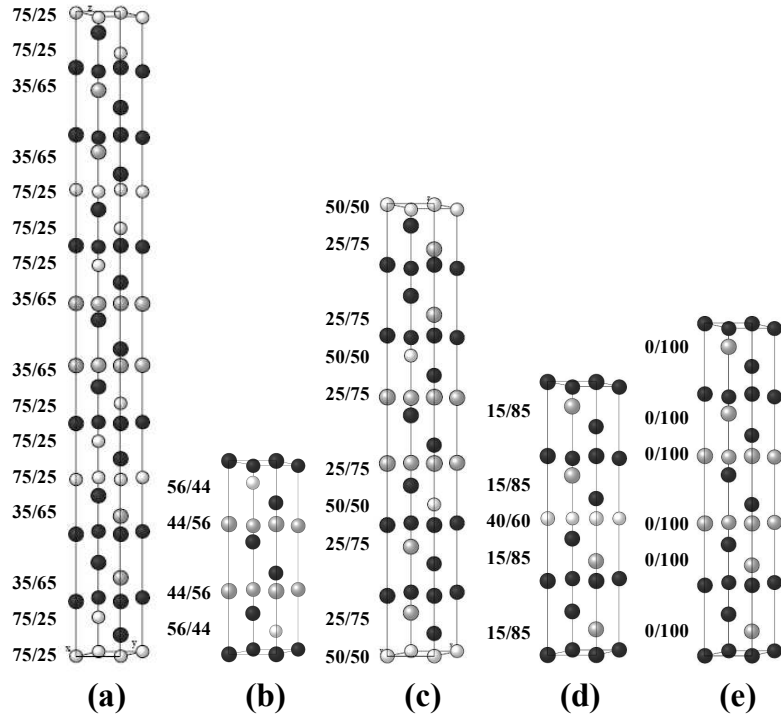
Fig. 4. Structures of the GeTe-Sb_2Te_3 homologous compounds which have so far been revealed using x-ray diffraction method. Large black and gray circles respectively indicate Te and Sb atoms, whereas small white ones represent Ge atoms. The atomic ratios of Ge and Sb (Ge/Sb) in the actual crystals are indicated beside each model. In these homologous structures, Te-Te consecutive layers are present in their layer stackings without exception.
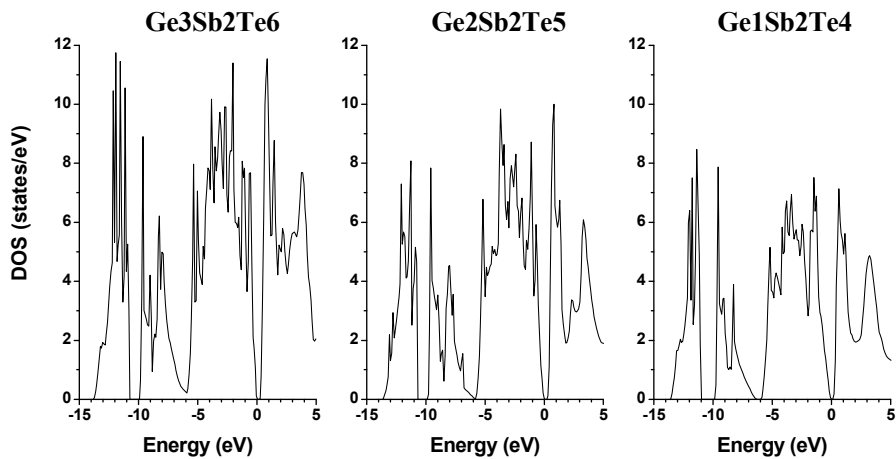

Fig. 5. DOS diagrams for $Ge_3Sb_2Te_6$, $Ge_2Sb_2Te_5$, and $Ge_1Sb_2Te_4$ obtained using band calculations. Fermi level corresponds to 0 eV. Calculations were performed on each structural model that had perfectly ordered atomic arrangement.

Biographyies

<u>Dr. Toshiyuki Matsunaga</u> received his Ph.D. in physics for his work on crystal structures, phase transitions, and bonding natures in intermetallic compounds in 1986 from Hiroshima University in Japan. 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.

Table of his education information

1974 - 1979	Yamaguchi University
1978	A Bachelor of Science
1979 - 1984	Hiroshima University (Graduate school)
1981	A Master of Science
1986	A Doctor of Science