

STRUCTURAL AND ELECTRICAL PROPERTIES OF OPTICAL PHASE-CHANGE MATERIALS GeTe AND Ge₈Sb₂Te₁₁

In a rewritable phase-change optical disk such as a digital versatile disc - random access memory (DVD-RAM), information is recorded using the change in optical property, such as reflectivity or transmissivity, that results from the phase transformation of the material between the crystal (erase) and amorphous (record) states [1]. Today, the GeTe-Sb₂Te₃ (GST) pseudobinary compound, typically Ge₈Sb₂Te₁₁ or Ge₂Sb₂Te₅, is the most widely used rewritable phase-change optical recording material. These materials are of considerable importance since compounds in this system are used not only for rewritable optical storage but also for future non-volatile electronic memories. However, the crystal structures and electrical properties of these materials have not been investigated in detail. We therefore investigated those of the two materials, GeTe and Ge₈Sb₂Te₁₁, by electric measurements, and X-ray powder diffraction and photoemission spectroscopy using synchrotron radiation at beamlines **BL02B2** and **BL47XU** [2].

GeTe and Ge₈Sb₂Te₁₁ have high- and low-temperature crystalline phases. The former phase has a NaCl-type cubic structure. Ge and Sb cations are located at the 4(*b*) site in the space group *Fm* $\bar{3}$ *m*; on the other hand, Te anions occupy the 4(*a*) site (see

Fig. 1). The latter phase has a rhombohedrally distorted NaCl-type structure (*R*3*m*), in which two kinds of ions migrate away from each other along the [111] axis, leaving the equilibrium positions, (0 0 0) and (1/2 1/2 1/2), that they had occupied in the high-temperature phase. Both compounds lie in these low-temperature phases at room temperature. The crystallographic data obtained by Rietveld analyses are shown in Table I, in which the *g*-parameter indicates the atom occupancy in each site. As seen in this table, a high density of about 2% Ge vacancies ($4 \times 10^{20}/\text{cm}^3$) was present at the Na sites in the GeTe crystal. This indicates that the single-phase region of the GeTe binary compound sits on the Te-rich side of the GST pseudobinary line in the Ge-Sb-Te ternary system [3]. On the other hand, the atomic occupation for the Ge₈Sb₂Te₁₁ compound was about (8+2)/11, which indicates that this compound contains almost no excess vacancies, and that its single-phase region lies on or very near the pseudobinary line.

It is known that in the GST pseudobinary NaCl-type structure, when its composition is exactly located on the pseudobinary line, the valence band is fully occupied by all the outermost electrons of the three kinds of constituent atoms; on the other hand, the conduction band is completely empty, irrespective of their compositions [4]. Figure 2 shows the electrical resistance measurement results for GeTe and Ge₈Sb₂Te₁₁ polycrystalline thin films undertaken at temperatures ranging from 4 - 280 K. It can be seen in this figure that the electrical resistivity obtained for GeTe has a positive correlation with temperature, showing fairly low values, which demonstrates that this film is a metal-like substance. On the other hand, the electrical resistance of the Ge₈Sb₂Te₁₁ film showed a slightly negative temperature dependence. This means that, unlike GeTe, Ge₈Sb₂Te₁₁ is a semiconducting substance. Our Hall effect measurements performed on the GeTe film at room temperature showed *p*-type electrical conductivity with a high carrier density of up to $5 \times 10^{20} \text{ cm}^{-3}$. We have revealed by molecular orbital calculation that Te atoms have received 0.30 electrons (/atom) from Ge atoms, and that this crystal tolerates an ionic bonding nature [2]. In other words, about 0.3 holes are formed per single Ge vacant site in the Madelung field to retain electrical neutrality, which means that the above-mentioned Ge vacancies present in the GeTe

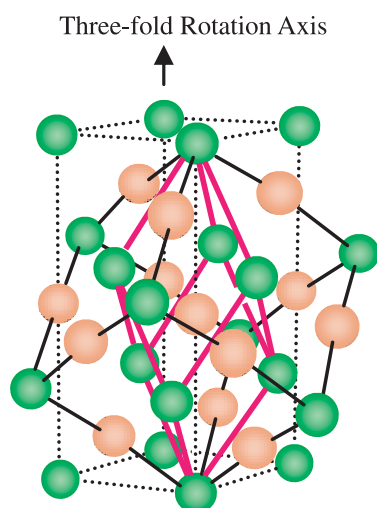


Fig. 1. Structure of GeTe or Ge₈Sb₂Te₁₁ low-temperature phase shown with both rhombohedral (thick lines —) and hexagonal (dotted lines •) unit cells. Green circles indicate Te atoms, whereas orange ones represent Ge/Sb atoms and vacancies. The NaCl-type cubic structure of the high-temperature phase, shown by thin solid lines, is slightly deformed in the low-temperature phase.

Industrial Applications

Table 1. Refined structural parameters for (a) GeTe and (b) $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ low-temperature phases at room temperature. Standard deviations are shown in parentheses. The final R -factors and lattice parameters for GeTe are $R_{\text{wp}} = 8.42\%$, $R_p = 5.81\%$, $R_1 = 1.29\%$, $R_{\text{wp}} \text{ expected} = 2.15\%$ and $a = 4.2806(4) \text{ \AA}$ and $\alpha = 58.259(5)^\circ$, respectively, and those for $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ are $R_{\text{wp}} = 4.03\%$, $R_p = 2.53\%$, $R_1 = 1.33\%$, $R_{\text{wp}} \text{ expected} = 2.88\%$ and $a = 4.2511(4) \text{ \AA}$ and $\alpha = 59.580(4)^\circ$, respectively.

(a) atom		site				(\AA^2)
Ge	1:1(a)	0.977(5)	0.5238(2)	x	x	1.52 (6)
Te	2:1(a)	1.0	0	0	0	0.74 (3)
(b) atom		site				(\AA^2)
$\text{Ge}_{8/11}\text{Sb}_{2/11}$	1:1(a)	1.024(3)	0.5154(4)	x	x	2.49 (5)
Te	2:1(a)	1.0	0	0	0	0.94 (2)

crystal can generate up to 1×10^{20} (electroconductive) holes $/\text{cm}^3$. This estimated density shows good agreement with the carrier density measured on our crystalline GeTe film. We therefore hold that this GeTe film is a metallic substance. The Hall effect measurement on the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ polycrystalline film showed that this substance has a lower carrier density (up to $1 \times 10^{19} \text{ cm}^{-1}$) at room temperature than GeTe. In addition, the measurement indicated that the carries had no clear polarity (positive or negative). We have clarified above that no excess vacancies are present in the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ crystal, unlike the GeTe crystal. In other words, the abovementioned interesting difference in electrical properties between GeTe and $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$, is decided by the presence of excess vacancies in these pseudo-binary crystals. The valence-band spectra obtained by the synchrotron radiation photoemission spectroscopy at room temperature are shown in Fig. 3. The energies are expressed in terms of the spectrometer Fermi level. As seen in the spectra, the top energies of the valence bands are different from each other; the

Fermi level in the GeTe spectrum lies at the top of the valence band, whereas that in $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ sits above it. These observations support our conclusion that the GeTe polycrystalline film is a metallic substance, but the film of the $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ pseudobinary polycrystalline compound is a semiconductor.

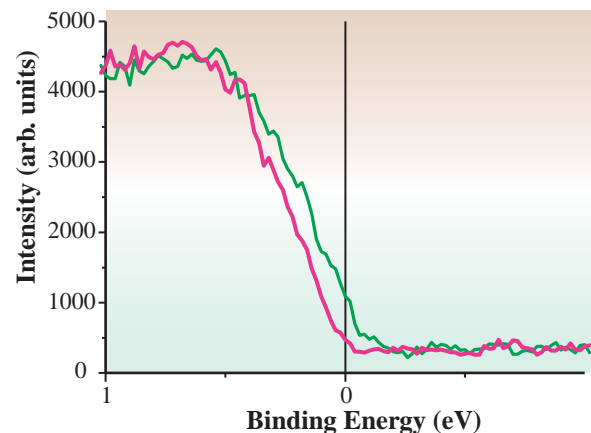


Fig. 3. Electron emission spectra near Fermi level of GeTe (green line) and $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ (pink line) crystalline films taken at room temperature by high-resolution hard X-ray photoemission spectroscopy.

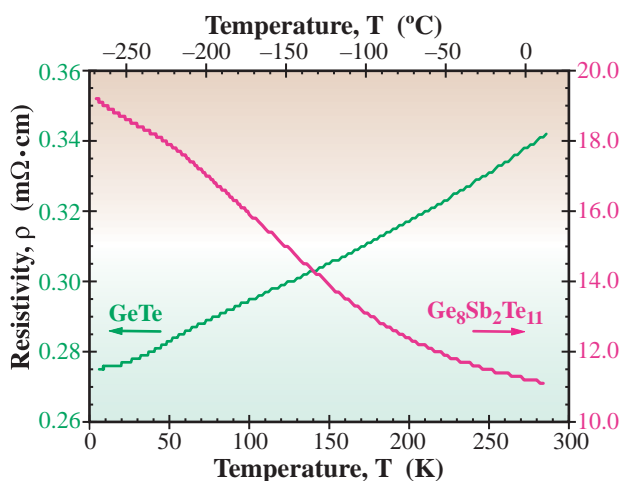


Fig. 2. Temperature dependence of electrical resistivity for GeTe (green line) and $\text{Ge}_8\text{Sb}_2\text{Te}_{11}$ (pink line) polycrystalline films.

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