

# Large displacement of germanium atoms in crystalline $\text{Ge}_2\text{Sb}_2\text{Te}_5$

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Local structure of NaCl-type crystalline  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  has been studied by the atomic pair distribution function analysis of pulsed neutron powder diffraction data. We have found the large displacement of germanium atoms in this crystalline phase. Usually, such a large lattice distortion has disadvantages for the electric conductivity. The electronic band structure, however, implies that this significant distortion in addition to the lattice defect at Na site reduces only thermal conductivity, while the highly ordered tellurium atoms at Cl site keep high electric conductivity. © 2005 American Institute of Physics. [DOI: 10.1063/1.1861976]

Phase change memory materials such as DVD-RAMs rapidly expand their markets for the recording of movies and television programs instead of video tapes. The compound  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  is one of the best materials for high-speed and high-rewritability.<sup>1</sup> The crystal structure study of related compounds becomes an important subject for the improvement of commercial performance. The compound  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  exhibits three different phases. They are a trigonal layered phase, a NaCl-type cubic crystalline phase,<sup>2</sup> and an amorphous insulating phase, which are characterized by the optical reflectivity.<sup>3</sup> The latter two phases have been prepared only as thin films. These two phases can be alternated within about 60 ns by laser irradiation. In the NaCl-type crystal structure, germanium, antimony, and vacancy sit randomly at Na site, while Cl site was entirely occupied by Te atom. Here, we report the atomic pair distribution function (PDF) analysis<sup>4</sup> of the crystalline cubic phase of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  (*c*- $\text{Ge}_2\text{Sb}_2\text{Te}_5$ ). This analysis needs wide reciprocal space measurement, which can be done by using intense source of spallation neutrons in addition to a large amount of sample.

The film samples with a thickness of approximately 1  $\mu\text{m}$  were prepared by sputtering on a silicon disk in Ar gas. The films were crystallized by means of laser irradiation and then scraped off with a spatula. About 5 g of powdered sample was sealed in a cylindrical vanadium tube. Neutron powder diffraction data were collected for 9 h at room temperature on the Neutron Powder Diffractometer NPDF<sup>5</sup> at the

Manuel Lujan Neutron Scattering Center of Los Alamos National Laboratory. The obtained data in the range of  $1.65 < Q < 35.0 \text{ \AA}^{-1}$  were corrected for experimental effects and normalized by standard data. This large  $Q_{\text{max}}$  leads to the high  $r$  resolution of our PDF data. For the present local structure analysis, PDFgetN<sup>6</sup> and PDFfit<sup>7</sup> programs were used while GSAS<sup>8</sup> was used for Rietveld average structure analysis. Hereafter we define average and local crystal structures as those determined by Rietveld and PDF analyses, respectively.

Experimental atomic pair distribution function,  $G(r)$ , was obtained by the Fourier transformation of the total structure function  $S(Q)$ , as follows:

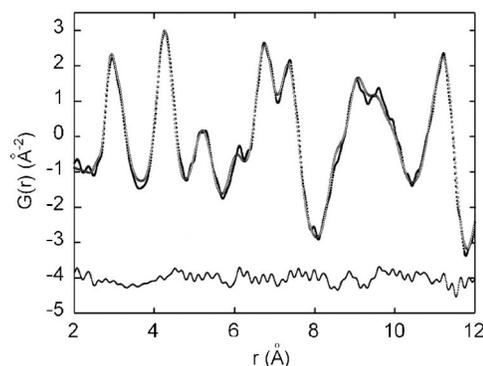


FIG. 1. Observed (closed circle), calculated (open circle), and difference (small closed circle) pair distribution function profiles in the fitted range of  $2 < r < 12 \text{ \AA}$ .

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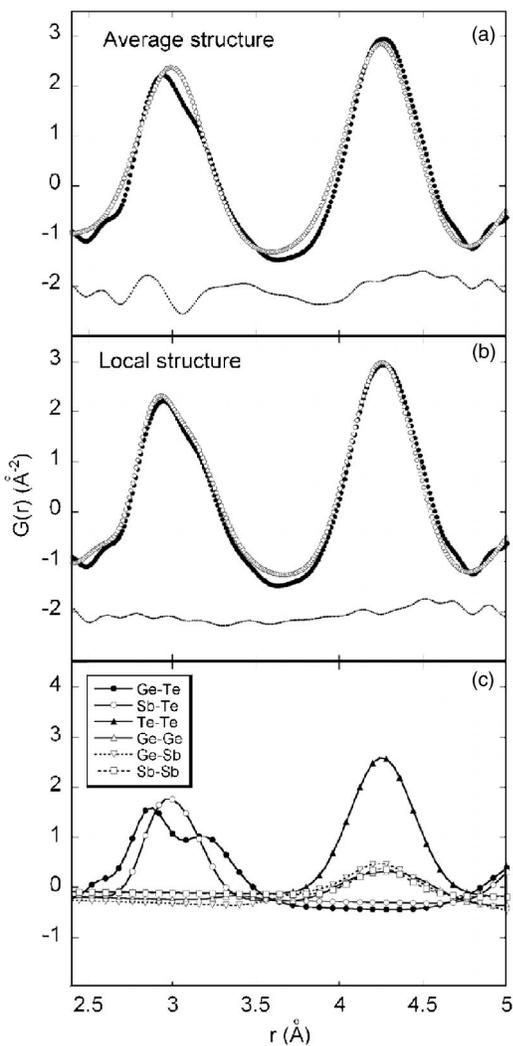


FIG. 2. Observed (closed circle), calculated (open circle), and difference (small closed circle) pair distribution function profiles for average (a) and local (b) structures in a short  $r$  range. Fitted  $G(r)$  components for local structure in (b) are shown in (c), indicating large displacement of germanium atoms.

$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ,$$

where  $\rho(r)$  is the microscopic pair density,  $\rho_0$  is the average number density, and  $Q$  is the magnitude of the scattering vector. The position and width of a peak in  $G(r)$  reflect the value and distribution of distances between different atomic correlations, and the peak area provides a measure of the corresponding coordination number.

If the average crystal structure was intrinsic, the first nearest neighbor peak in the  $G(r)$  should be a broad simple Gaussian. Figure 1 shows observed, calculated, and difference of  $G(r)$  for the average and the local crystal structures. As shown in Fig. 2, the observed first nearest neighbor peak had a complex structure. It cannot be described by one broad peak expected from the average structure. Since Cl site is entirely occupied by Te,<sup>3</sup> only Ge-Te and Sb-Te atomic correlations appear in the first peak. Note that the coherence scattering lengths of Ge, Sb, and Te are 8.19(2), 5.57(3), and 5.68(2) fm, respectively. Ge atoms have dominant contribution in this neutron scattering measurement. The  $G(r)$  pattern in the real space range of  $2.0 < r < 12.0$   $\text{\AA}$  was fitted under

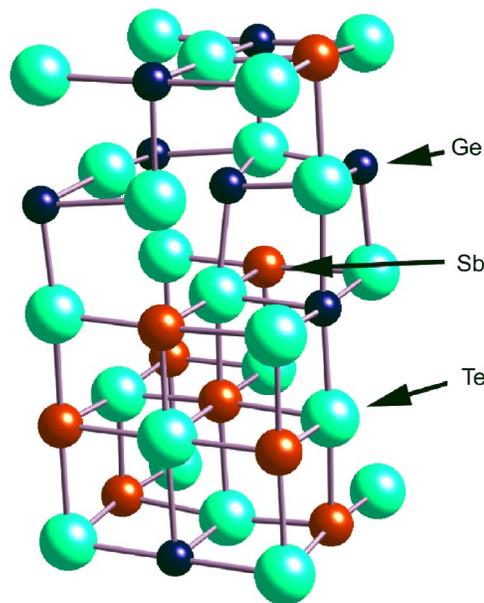


FIG. 3. (Color online) Local crystal structure of  $c\text{-Ge}_2\text{Sb}_2\text{Te}_5$ . Only bonds shorter than 3.2  $\text{\AA}$  are shown.

the following restriction. We set a periodic nonsymmetric cubic unit cell with eight sites, where one Te atom was fixed at the origin. All Te occupation factors were fixed to be unity, while the summation of occupation factors of Ge and Sb atoms at Na site was fixed to be an average value of 0.8. Isotropic thermal factors were assumed to depend only on the elements. Otherwise, all atoms were freely displaced. The obtained distorted crystal structure is shown in Fig. 3. By this refinement, the  $R_{\text{wp}}$  factor decreased from 14.0% in the case of average structure to 10.8%. If we set Sb atoms displaced from Na position like Ge as initial parameters for PDF refinement, the  $R_{\text{wp}}$  factor increased to 12.1%, because of a local minimum of least square refinement.

As shown in Fig. 2(c), Ge-Te bond lengths of 3.03(22)  $\text{\AA}$  have much wider distribution than Sb-Te bond lengths of 3.02(10)  $\text{\AA}$ , where numbers in parentheses are estimated standard deviations of the last digits. The wide and split Ge-Te correlation peak would be due to the narrower radius of Ge 4p orbital than Sb 5p orbital. As a whole, large displacement of Ge atoms is characteristic in the crystal structure.

The obtained crystallographic parameters were consistent with the following previous results. In an amorphous solid of PdGeSbTe, the nearest neighbor bond lengths for Ge-Te and Sb-Te are 2.61 and 2.84  $\text{\AA}$ , respectively.<sup>9</sup> The bond length of Ge-Te (2.65  $\text{\AA}$ ) in amorphous GeTe is much shorter than that (2.80  $\text{\AA}$ ) in the crystalline sample,<sup>10</sup> whereas the bond length of Sb-Te (2.86  $\text{\AA}$ ) in the amorphous Sb<sub>2</sub>Te<sub>3</sub> is close to that (2.89  $\text{\AA}$ ) in the crystal.<sup>11</sup> These results also support our result of large displacement of germanium atoms.<sup>12</sup>

The present compound exhibits metal-like  $p$ -type conductivity.<sup>13</sup> The electronic bands around the Fermi energy were mainly composed of  $p$  orbitals, which split into conduction and valence bands similar to GeTe band structure.<sup>14,15</sup> Because of the electronegativity, the occupied valence bands are mainly made of 5p orbital of Te anions, where there is little lattice distortion and no defects. The weak electron affinity of Ge at Na site also reduces Ge con-

tribution to the valence bands. Therefore, the present electronic conduction is little affected by the present Ge local lattice distortion. On the contrary, the lattice distortion reduces the thermal conductivity significantly. The thermal conductivity is expressed by phonon and electronic terms as follows:

$$\kappa = \frac{1}{3}C_{\text{ph}}v_{\text{ph}}l_{\text{ph}} + \frac{1}{3}C_{\text{el}}v_{\text{el}}l_{\text{el}},$$

where  $C$  is the specific heat,  $v$  is the velocity,  $l$  is the mean free path, and the subscripts of ph and el are phonon and electron, respectively.

The second electronic term in the thermal conductivity is negligible in comparison with the first large phonon term, because of the small carrier density in  $c$ -Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub>. Originally the heavy elements such as Sb and Te in this compound decrease the phonon group velocity,  $v_{\text{ph}}$ . In addition, the present local lattice distortion and the lattice defect reduce the phonon mean free path down to the lattice constant, leading to the significant decrease of thermal conductivity. This helps to limit the thermal diffusion under laser irradiation, similar to the amorphous case. According to this finding, it can be concluded that doping of various heavy cations such as Bi at Na site can reduce thermal conductivity without decreasing the electric conductivity. This finding can be applied to thermoelectric materials. They also require low thermal conductivity and high electric conductivity, simultaneously.<sup>16</sup> Present result indicates that the sputtering method could be a useful synthetic way for disordered thermoelectric materials such as Ge–Bi–Te.<sup>17</sup>

In conclusion, we have found large displacement of Ge atoms at Na site in NaCl-type  $c$ -Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> by the PDF analysis of neutron powder diffraction data. In terms of the electronic band structure, this finding suggests individual rules at Na and Cl sites. In other words, site selective disorder can reduce thermal conductivity while keeping high electric conductivity.

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