

## Pressure-induced phase transition of $\text{Bi}_2\text{Te}_3$ to a bcc structure

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(Received 8 December 2010; revised manuscript received 15 January 2011; published 17 March 2011)

The pressure-induced phase transition of bismuth telluride,  $\text{Bi}_2\text{Te}_3$ , has been studied by synchrotron x-ray diffraction measurements at room temperature using a diamond-anvil cell (DAC) with loading pressures up to 29.8 GPa. We found a high-pressure body-centered cubic (bcc) phase in  $\text{Bi}_2\text{Te}_3$  at 25.2 GPa, which is denoted as phase IV, and this phase appears above 14.5 GPa. Upon releasing the pressure from 29.8 GPa, the diffraction pattern changes with pressure hysteresis. The original rhombohedral phase is recovered at 2.43 GPa. The bcc structure can explain the phase IV peaks. We assumed that the structural model of phase IV is analogous to a substitutional binary alloy; the Bi and Te atoms are distributed in the bcc-lattice sites with space group  $Im\bar{3}m$ . The results of a Rietveld analysis based on this model agree well with both the experimental data and calculated results. Therefore, the structure of phase IV in  $\text{Bi}_2\text{Te}_3$  can be explained by a solid solution with a bcc lattice in the Bi-Te (60 atomic % tellurium) binary system.

DOI: [10.1103/PhysRevB.83.092102](https://doi.org/10.1103/PhysRevB.83.092102)

PACS number(s): 62.50.-p, 61.50.Ks, 61.05.cp, 07.35.+k

Bismuth telluride,  $\text{Bi}_2\text{Te}_3$ , is a typical thermoelectric material with a high-performance near room temperature.<sup>1-3</sup>  $\text{Bi}_2\text{Te}_3$  has a rhombohedral structure with the space group  $R\bar{3}m$ , which is denoted as phase I; the hexagonal unit-cell parameters are  $a_0 = 4.395 \text{ \AA}$  and  $c_0 = 30.44 \text{ \AA}$  at ambient pressure and temperature.<sup>4</sup> Bulk  $\text{Bi}_2\text{Te}_3$  has a relatively narrow band gap of 0.171 eV<sup>5</sup> and a high density of states near the Fermi level. Upon applying pressure, these characters are expected to cause metallization and superconductivity.<sup>5-12</sup> Several groups have reported pressure-induced superconductivity.<sup>9-14</sup> In our previous study under hydrostatic pressure, the onset temperature of the superconducting transition  $T_c^{\text{onset}}$  is 2.7 K at 9.0 GPa. As the pressure increases,  $T_c^{\text{onset}}$  decreases up to 10 GPa, but greatly increases from 10 to 13 GPa:  $T_c^{\text{onset}} = 5.0 \text{ K}$  at 13 GPa.<sup>12</sup>

High-pressure x-ray diffraction studies have shown that the structural phase transition from phase I to phase II occurs around 8 GPa.<sup>11,15</sup> Phase II coexists with phase III at pressures above 14 GPa with helium as pressure transmitting medium.<sup>11</sup> The crystal structures of phase II and III have yet to be determined. Jacobsen *et al.* have performed x-ray diffraction measurements using an ethanol-methanol mixture as a transmitting medium and found that the phase II crystal has orthorhombic  $I222$  symmetry.<sup>15</sup> Compared to the structural changes under high pressure, the negative and positive pressure dependencies of  $T_c$  are assumed to be due to phase II and phase III, respectively.<sup>12</sup>

Furthermore, a recent theoretical study predicted that  $\text{Bi}_2\text{Te}_3$ , bismuth selenide  $\text{Bi}_2\text{Se}_3$ , and bismuth-antimony binary alloy  $\text{Bi}_{1-x}\text{Sb}_x$  would be candidates for three-dimensional topological insulators,<sup>16</sup> and they have been experimentally established.<sup>17</sup> Since then,  $\text{Bi}_2\text{Te}_3$  has attracted much attention in basic and applied research. Recently, we have performed additional x-ray diffraction measurements under hydrostatic pressure up to 30 GPa to reveal the structure at higher pressures. In this experiment, the phase transition to another high-pressure phase, which has body-centered

cubic structure, was observed. Herein we report the high-pressure bcc phase and discuss its crystal structure. The crystal structures of phase II and phase III are still under investigation.

The sample was a lump of polycrystalline  $\text{Bi}_2\text{Te}_3$  (99.99% purity, Kojundo Chemical Lab. Co., Ltd.), which was cooled by liquid nitrogen in an alumina mortar and subsequently ground into a fine powder over 10 hours under nitrogen gas. The sample was pressurized using a diamond anvil cell (DAC) assembled by a pair of diamond anvils with 0.3 mm culet diameter and 2 mm anvil height. The indentation technique using the anvil culet surface reduced the rhenium gasket thickness from 150  $\mu\text{m}$  to 45  $\mu\text{m}$ . The sample chamber was prepared by drilling a 160  $\mu\text{m}$  diameter hole at the center of the indentation on the gasket. The powdered sample was placed in the chamber with ruby balls ( $\sim 10 \mu\text{m}$  in diameter) as a pressure marker.<sup>18</sup> Then the chamber was filled with high-density helium gas as the pressure-transmitting medium, which was compressed up to 180 MPa at room temperature by a gas loading system.<sup>19</sup>

Angle-dispersive powder x-ray diffraction measurements were carried out in beamline BL-18C of the Photon Factory in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The sample in the DAC was irradiated using synchrotron radiation beams monochromatized to an energy of 25.6 keV ( $\lambda \approx 0.4840 \text{ \AA}$ ) through a pinhole collimator with a 40  $\mu\text{m}$  in diameter. Each diffraction pattern was recorded using an imaging plate (200 mm  $\times$  250 mm area) with an exposure time between 120 and 540 minutes upon compression up to 29.8 GPa and upon decompression at room temperature.

Figure 1 shows the x-ray diffraction patterns of  $\text{Bi}_2\text{Te}_3$ . All the reflections obtained at 0.61 GPa are explained by space group  $R\bar{3}m$  with lattice parameters of  $a = 4.366(0) \text{ \AA}$  and  $c = 30.11(0) \text{ \AA}$ . The reflections from phase II<sup>11</sup> are observed at pressure above 8.41 GPa. These intensities are enhanced under pressure up to about 20 GPa. After the transition from phase I to phase II, we found small reflections, which are marked by  $\nabla$  and  $\downarrow$  at pressure above 14.5 GPa in Fig. 1 and

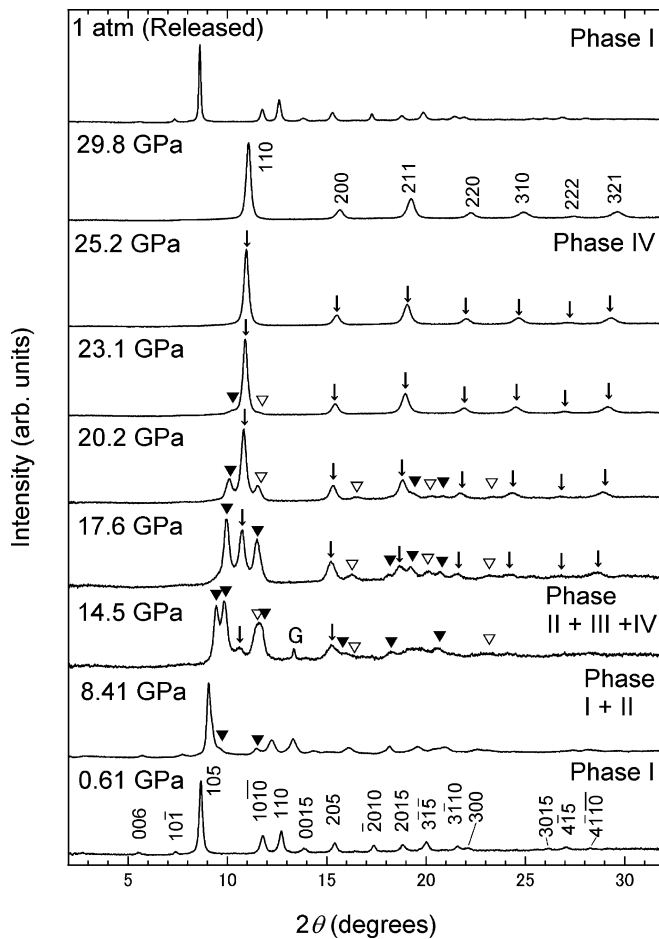


FIG. 1. X-ray diffraction patterns of  $\text{Bi}_2\text{Te}_3$  under pressure up to 29.8 GPa at room temperature. Arrows indicate reflection of phase IV. Closed and open triangles indicate reflections of phases II and III, respectively. Top pattern was observed at ambient pressure after releasing pressure. Letter G denotes reflection from gasket.

differ from the phase II reflections. From the changes in the patterns, reflections  $\nabla$  and  $\downarrow$  are assigned to be phase III<sup>11</sup> and another high-pressure phase, phase IV, respectively. This mixed-phase state continues to 23.1 GPa. However, the crystal structure transforms to the high-symmetry one at pressures above 25.2 GPa; a single phase assigned to a cubic system, phase IV, is obtained. As the pressure decreases from 29.8 GPa, the diffraction patterns exhibit the opposite change with a pressure hysteresis. At 10.3 GPa, phases II and III reappear, and the original rhombohedral phase I reappears at 2.43 GPa. As shown in the top of Fig. 1, phase I is completely recovered upon releasing the pressure.

A body-centered cubic (bcc) structure can explain the peaks from phase IV obtained at 25.2 GPa. Except for the bcc-phase peaks, extra reflections are not present [Fig. 2(a)], suggesting that the structural model of phase IV is analogous to substitutional binary alloys; the Bi and Te atoms with their original concentrations are arranged in the bcc sites. For structural refinement, we assumed that the structure of phase IV has a probability of Bi 40% and Te 60% atoms and that the atoms are arranged in the bcc-lattice sites with space group  $Im\bar{3}m$ . Rietveld refinement of phase IV was performed for the

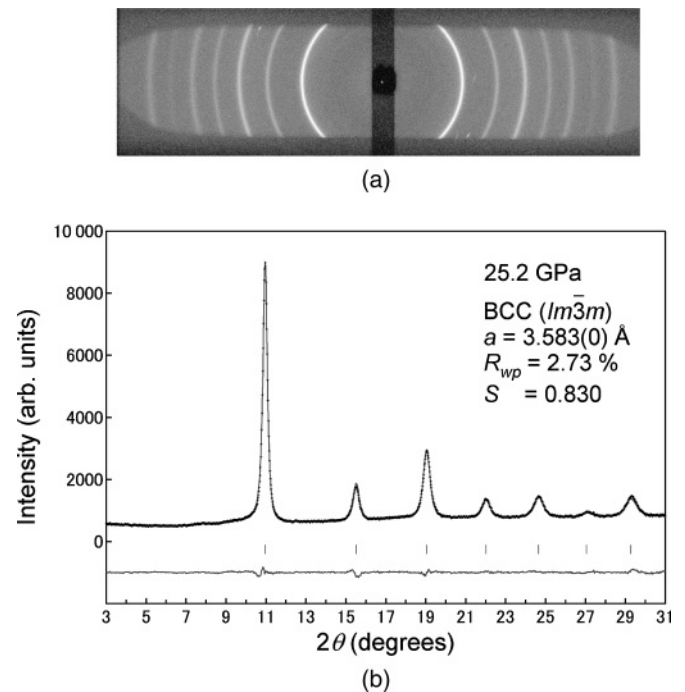


FIG. 2. (a) Powder diffraction images of  $\text{Bi}_2\text{Te}_3$  at 25.2 GPa recorded on an imaging plate. The spot in the diffraction image comes from Kossel lines of the diamond anvil, which were removed by image processing. (b) Result of Rietveld analysis of  $\text{Bi}_2\text{Te}_3$  at 25.2 GPa. Dots and solid line represent the observed and calculated intensities, respectively. Ticks below the profile mark the positions of the reflections from the bcc lattice. Solid line at the bottom shows the residual error.

diffraction patterns obtained at 23.1, 25.2, 27.4, and 29.8 GPa using the RIETAN-2000 program.<sup>20,21</sup> In the present analysis, the calculated patterns agree well with the experimental ones:  $R_{wp} = 2.75\%$  and  $S = 1.12$  at 23.1 GPa as the maximum values. Figure 2(b) shows the results of the Rietveld analysis for the diffraction pattern obtained at 25.2 GPa with  $R$  factor

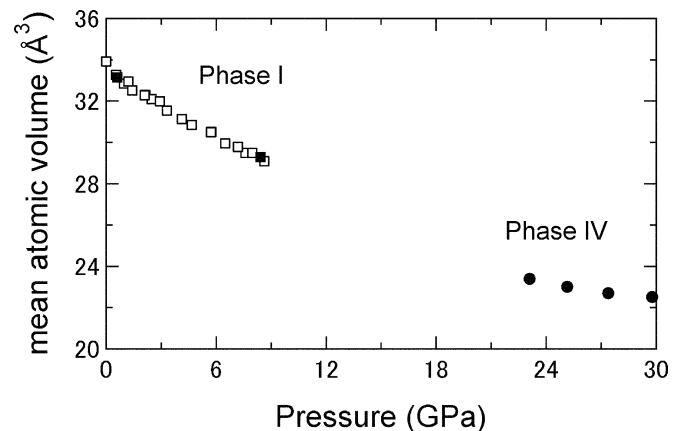


FIG. 3. Pressure dependence of the atomic volume for phases I and IV. Closed circles indicate the atomic volume of phase IV. Closed and open squares indicate the atomic volume of the present and previous data of phase I, respectively. Pressure dependence of the atomic volume for phase II and phase III have not been obtained since the crystal structures have yet to be determined.

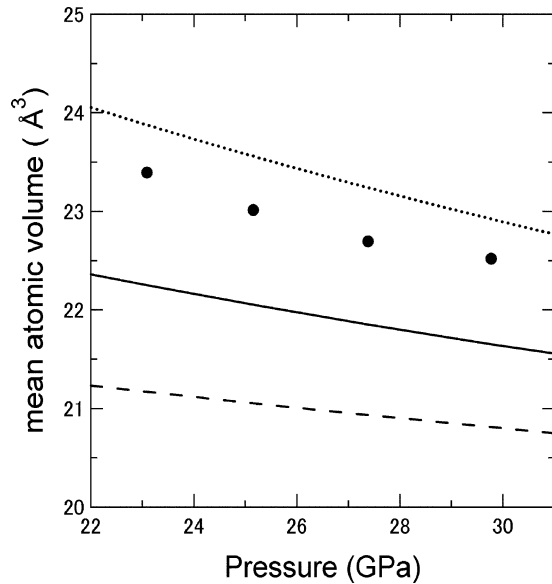


FIG. 4. Pressure dependence of the atomic volume for high-pressure bcc phase of  $\text{Bi}_2\text{Te}_3$ , Bi, and Te. Closed circles are experimentally observed  $\text{Bi}_2\text{Te}_3$ . Solid lines are estimated from Vegard's law. Dotted line is from Ref. 24 for Bi. Dashed line is from Ref. 25 for Te.

$R_{\text{wp}} = 2.73\%$  and  $S = 0.830$ , yielding a lattice constant of  $a = 3.583(0)$  Å. Therefore, we determined that the structure of phase IV in  $\text{Bi}_2\text{Te}_3$  can be explained by a solid solution with a bcc lattice in the Bi-Te binary system. Figure 3 shows the pressure change with atomic volume in phase IV. The atomic volume continuously decreases with increasing pressure. At 29.8 GPa, the atomic volume reaches 66.4% of the original volume at ambient pressure. Pressure dependence of the atomic volumes for phase II and phase III has not been obtained since the crystal structures have yet to be determined.

We evaluated the homogeneity of the bcc-solid solution in the Bi-Te system through Vegard's law,<sup>22,23</sup> which is an empirical rule to explain the character of a solid solution. The law holds that a linear relation, which can be explained by a hard sphere model,<sup>23</sup> exists between the lattice constant of an alloy and the concentrations of the constituent elements at a constant temperature.<sup>22</sup> As with  $\text{Bi}_2\text{Te}_3$ , the crystal structures of pure bismuth and tellurium also exhibit high-pressure bcc phases.<sup>24,25</sup> Therefore, we compared the atomic volume of  $\text{Bi}_2\text{Te}_3$  obtained experimentally ( $V_{\text{exp}}$ ) to that estimated from Vegard's law ( $V_{\text{Vegard}}$ ) using the atomic volumes of the high-pressure bcc phase in pure bismuth and tellurium. We estimated  $V_{\text{Vegard}}$  from a linear interpolation between pure bismuth and tellurium as a solid solution of 60 atomic % tellurium concentration. Each atomic volume of the bcc phase

in pure bismuth and tellurium was estimated by interpolation and extrapolation using first-order Murnaghan and Vinet equations of state, respectively, reported in previous studies.<sup>24,25</sup> As shown in Fig. 4, we compared  $V_{\text{exp}}$  to the atomic volumes of pure bismuth and tellurium, and to  $V_{\text{Vegard}}$  under high pressure.  $V_{\text{exp}}$  greatly deviates from  $V_{\text{Vegard}}$  and is larger than  $V_{\text{Vegard}}$  at each pressure: The estimated deviation ( $V_{\text{dev}}$ ) is 4.873% as the maximum value when the deviation is defined as  $V_{\text{dev}} = 1 - V_{\text{Vegard}}/V_{\text{exp}}$ . At ambient pressure, the lattice constants and tellurium concentration have been compared in a metastable solid solution containing up to 50 atomic % tellurium by an ultrahigh cooling rate of the melt.<sup>26</sup> In the concentrate region, the experimentally obtained atomic volume is larger than one estimated from the hard-sphere model. Meanwhile, the bismuth-antimony alloy  $\text{Bi}_{1-x}\text{Sb}_x$ , which is a typical binary complete solid solution, shows a linear behavior with Vegard's law at ambient conditions. Additionally,  $\text{Bi}_{1-x}\text{Sb}_x$  forms the bcc structure under high pressure; the phase transition to the bcc structure occurs at 12 GPa for  $x = 0.15$ .<sup>27,28</sup> Furthermore, we have clearly shown that the atomic volume of  $\text{Bi}_{0.85}\text{Sb}_{0.15}$  follows Vegard's law under high pressure.<sup>27</sup>

At ambient pressure,  $\text{Bi}_{1-x}\text{Sb}_x$ , which is composed of elements in the 15th group of the periodic table, forms covalent bonds.<sup>29</sup> On the other hand, in  $\text{Bi}_2\text{Te}_3$ , which is composed of elements in the 15th and 16th groups, the covalent bonds have an ionic component along Bi-Te bonds, which causes the bonds to be stronger than normal covalent bonds.<sup>30</sup> Therefore, we infer that the deviation from Vegard's law in phase IV of  $\text{Bi}_2\text{Te}_3$  is due to the remaining strong ionic-covalent bonds in the pressure region of phase IV. Upon further compression, the ionic-covalent bonds should disappear, and the atomic volume of  $\text{Bi}_2\text{Te}_3$  will obey Vegard's law.

In summary, synchrotron-radiation x-ray diffraction measurements were used to investigate the high-pressure structural phase of  $\text{Bi}_2\text{Te}_3$  up to 29.8 GPa. We found a high-pressure bcc phase in  $\text{Bi}_2\text{Te}_3$  at 25.2 GPa. The structure of phase IV is explained by a solid solution with a bcc lattice in space group  $Im\bar{3}m$  for a Bi-Te binary system; the Bi and Te atoms are distributed in the bcc-lattice sites. Due to the remaining strong ionic-covalent bonds up to 29.8 GPa, the relation between the atomic volume and concentration of the constituent elements deviates from Vegard's law.

The present work was concluded under Proposal No. 2009G656 of the Photon Factory. This research was partially supported by Grants-in-Aid for Science Research on Priority Areas: Novel State of Matter Induced by Frustration No. 20046006, and New Materials Science Using Regulated Nano Space-Strategy in Ubiquitous Elements, No. 20045003, from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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