Substitutional Alloy of Bi and Te at High Pressure

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Being a best known thermoelectric material and a topological insulator at ambient condition, magic bismuth telluride (Bi_2Te_3) under pressure transforms into several superconducting phases, whose structures remain unsolved for decades. Here, we have solved the two long-puzzling low high-pressure phases as seven- and eightfold monoclinic structures, respectively, through particle-swarm optimization technique on crystal structure prediction. Above 14.4 GPa, we experimentally discovered that Bi_2Te_3 unexpectedly develops into a Bi-Te substitutional alloy by adopting a body-centered cubic disordered structure stable at least up to 52.1 GPa. The continuously monoclinic distortion leads to the ultimate formation of the Bi-Te alloy, which is attributed to the Bi \rightarrow Te charge transfer under pressure. Our research provides a route to find alloys made of nonmetallic elements for a variety of applications.

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Alloys can have greater superior physical properties than each individual end member and have been widely used for engineering and industry. One of the most common types of alloy is a substitutional crystalline solid solution in which atoms of one element randomly substitute for atoms of another element. The search for new alloys is one of the major scientific tasks and thus attracts a lot of attention. Substitutional alloys are usually made by elemental metals (e.g., Au-Cu, Au-Ag, Zn-Cu, etc) and restricted by the Hume-Rothery rules [1]. There are fewer reports on the synthesis of substitutional alloys from nonmetallic elements. Exploration of matter at extreme conditions is a central theme in a broad range of scientific disciplines. The application of pressure can induce significant changes in atomic and electronic structures, which allows tuning the atomic structure and the very nature of chemical bonds to produce novel materials. Here, we report that a Bi-Te substitutional alloy can be synthesized by pressurizing Bi₂Te₃, a stoichiometric semiconductor.

Under atmospheric pressure, Bi₂Te₃ crystallizes in the rhombohedral R-3m structure (α -Bi₂Te₃, phase I) which is known to exhibit excellent thermoelectric properties (see, e.g., Ref. [2]). Recently, Bi₂Te₃ and related compounds (Bi₂Se₃ and Sb₂Te₃) are even reported as the simplest three-dimensional topological insulators [3,4]. Pressure can induce significant changes in the crystal and electronic structures of Bi2Te3. For example, Kullmann et al. reported effects of hydrostatic and uniaxial pressures on Bi₂Te₃ [5] and a pressure-induced giant improvement of thermoelectric power factor was observed at 1 GPa [2]. In 1972, Bi₂Te₃ was found to experience structural phase transitions [6] into superconductors ($T_c = 4.3$ K at 7.1 GPa) [7] under pressure. Until recently, high-pressure (HP) x-ray diffraction (XRD) experiments [8,9] demonstrated that α -Bi₂Te₃ transits into HP phases II and III at 8.0 and 14.0 GPa, respectively. Very recently, Bi_2Te_3 was remarkably reported as a possible topological superconductor able to generate Majorana fermions [10] within phase I and was found to transform into several superconducting phases with a highest T_c of 9.5 K under pressure [10–12], but the crystal structures as the key to understand the intriguing HP behavior of Bi_2Te_3 have remained elusive for several decades.

We have investigated the HP structures of Bi_2Te_3 by a joint theoretical and experimental study. The theoretical research involves an application of our newly developed crystal structural prediction technique through the particle swarm optimization (PSO) algorithm, requiring only chemical compositions for a given compound to predict stable or metastable structures at given external conditions (e.g., pressure) [13]. Simulations and XRD experiments unraveled that low HP phases II and III adopt monoclinic sevenfold C2/m and eightfold C2/c structures, respectively. At higher pressures, >14.4 GPa, we have discovered a unexpected formation of a substitutional alloy stable at least up to 52.1 GPa.

Our PSO methodology [13] on crystal structural prediction has been implemented in CALYPSO code [14] and successfully applied to the prediction of several HP structures [13,15,16]. The underlying *ab initio* structural relaxations and electronic calculations were carried out using density functional theory within the Perdew-Burke-Ernzerhof exchange-correlation as implemented in the VASP code [17]. The PAW pseudopotential with $6s^26p^3$ and $5s^25p^4$ electrons as valence for Bi and Te, respectively, was adopted. The energy cutoff 300 eV and appropriate Monkhorst-Pack *k* meshes were chosen to ensure that enthalpy calculations are well converged to better than 1 meV/atom. To calculate the electronic charge and atomic volume, we used the Bader charge analysis [18] obtained within a grid of $640 \times 640 \times 640$. The phonon calculations were carried out by using a supercell approach [19] as implemented in the PHONOPY code [20].

Commercially available Bi2Te3 powder (Alfa Aesar, 99.999%) was loaded into a hole of 90 μ m diameter in a stainless-stell compressible gasket and compressed between two 300 μ m culets diamond anvils. Pressure determination was achieved by the ruby scale [21]. The methanol-ethanol (4:1) mixture was used as the pressure transmitting medium. In situ high-pressure XRD spectra were measured up to 52.1 GPa using angle-dispersive XRD source ($\lambda = 0.3866$ Å) at beam line X17B3 of the National Synchrotron Light Source at Brookhaven. The Bragg diffraction rings were recorded with an imaging plate detector. Average acquisition time was 300 s. The two-dimensional diffraction images were analyzed using the FIT2D software, yielding one-dimensional intensity versus diffraction angle 2θ patterns. HP synchrotron x-ray patterns were fitted by Rietveld profile matching through the GSAS + EXPGUI programs [22].

Structure predictions were performed in the pressure range 0-50 GPa with 1-4 f.u. per simulation cell. Below 10 GPa, we found the most stable structure is the experimental α -Bi₂Te₃ [Fig. 1(a)], validating our method adopted here. We uncovered a group of new structures under higher pressure. Among them, three monoclinic structures all having 4 f.u./cell were found to be most stable at certain pressure ranges. A layered monoclinic sevenfold C2/m structure (β -Bi₂Te₃) [23] was found at 12 GPa. Polyhedral views of β -Bi₂Te₃ [Fig. 1(b)] reveal Te-Bi-Te sandwiches stacking order similar to that in α -Bi₂Te₃. But there are seven Te ions as ligand atoms, in stark contrast to the six-coordinated α -Bi₂Te₃. At 14 GPa, a three-dimensional monoclinic C2/c structure [γ -Bi₂Te₃, Fig. 1(c)] was predicted. Interestingly, γ -Bi₂Te₃ is an eight-fold structure formed by BiTe₈ hendecahedrons consisting of two-face capped trigonal prisms. Above 16 GPa, we find another compact monoclinic C2/m structure [Fig. 1(d)]. Here, Bi ions are centered in either enneahedrons or dodecahedrons to form nine- or tenfold bonding with Te. The BiTe₉/BiTe₁₀ polyhedrons can be viewed as



FIG. 1 (color online). Polyhedral views of (a) α -Bi₂Te₃, (b) β -Bi₂Te₃, (c) γ -Bi₂Te₃ and (d) nine/ten-fold *C*2/*m* structures. The dashed lines denote the unit cells and the large and small spheres represent Bi and Te atoms, respectively.

bcc cells with one or two extra Te ions located on the top of the cells. The calculated enthalpy curves (relative to α -Bi₂Te₃, Fig. 2) for various structures confirm the energetic stability of our predicted structures. Phonon calculations established the dynamical stabilities of these predicted structures in view of the absence of imaginary frequencies [23]. Our predicted β - and γ -Bi₂Te₃ structures correspond to the HP phases II and III [8,9]. The predicted nine or tenfold C2/m structure is an indication of new phase IV.

We have then performed HP XRD experiments in pressure steps of 1–2 GPa on Bi₂Te₃ via a diamond-anvil cell. Selected diffraction patterns are shown in Fig. 3. At ambient condition, all the diffraction peaks can be indexed to the ambient α -Bi₂Te₃ structure (a = 4.383 Å and c = 30.487 Å) by the Rietveld refinement. At 8.2 and 13.4 GPa, we observed two HP phases II and III, where the measured XRD patterns are in excellent agreement



FIG. 2 (color online). (a) Enthalpy curves (relative to α -Bi₂Te₃) of various structures as function of pressure in Bi₂Te₃. Enthalpies are given per formula unit. (b) Experimental volume versus pressure data for phases I–IV. Results for phase I from Ref. [9] are also shown for comparison. Obvious volume drops are evidenced to characterize the first-order I \rightarrow II \rightarrow III \rightarrow IV transitions.



FIG. 3 (color online). XRD patterns collected at various pressures for Bi₂Te₃ with an incident wavelength $\lambda = 0.3866$ Å. The peaks marked as asterisks, solid circles, and solid triangles are the diffraction peaks for phases II, III, and IV, respectively.

with the earlier XRD data [9]. Note that phase III can only stabilize in a narrow pressure range and coexists with either phase II or IV in the whole pressure range. At 14.4 GPa phase III starts to transit into a new phase IV. Above 25 GPa, the transformation is complete and no further transition is observed up to 52.1 GPa. The phase transitions are reversible. After a full pressure release, Bi_2Te_3 was recovered to the ambient-pressure structure (see the top spectrum of Fig. 3). It is worth noting that the used methanol-ethanol mixture as the pressure transmitting medium can result in quasi(non)-hydrostatic effects above 10 GPa [23], leading to lower transition pressures than those in Ref. [9].

We point out that using the sole experimental XRD data, HP structures II and III are hardly solved through Rietveld refinement. This explains why these structures remain unknown for several decades [6]. We blindly compared the simulated XRD patterns of β - and γ -Bi₂Te₃ with the observed data for phases II and III [23]. The mutual agreements encourage us to perform subsequent fine Rietveld analyses on our experimental data by use of the predicted structures. Excellent Rietveld fittings [Figs. 4(a) and 4(b)] between experimental and theoretical profiles enable us to unambiguously determine the crystal structures of phases II and III as β - and γ -Bi₂Te₃, respectively.

The experimental XRD pattern of phase IV is simple and can be indexed to a bcc unit cell (occupancy: 0.4 for Bi and 0.6 for Te) by Rietveld refinement [Fig. 4(c)]. This cubic phase strictly follows the extinction rules for space group Im-3m, and this determination leads to a = 3.571 Å, allowing only one inequivalent atomic position at 2a (0, 0, 0). Within this structure, Bi and Te atoms are disordered to



FIG. 4 (color online). The diffraction profiles of high-pressure phases of Bi_2Te_3 at (a) 12.6 GPa, (b) 14.4 GPa, and (c) 25.8 GPa, respectively. The solid lines and open circles represent the Rietveld fits for the lattice and observed data, respectively, and the solid lines at the bottom are the residual intensities. The vertical bars indicate the peak positions. Diffraction patterns in (b) are a mixture of phases III, II, and IV, whose XRD peaks are indicated by the first-, second-, and third-row vertical bars, respectively.

randomly share the bcc lattice sites, forming a Bi-Te substitutional alloy. Intuitively, it is not easy to understand the formation mechanism of this Bi-Te alloy since the atomic radii of Bi and Te atoms ($r_{\text{Bi}} = 1.43$ Å, $r_{\text{Te}} = 1.23$ Å) have large difference at ambient pressure though satisfying the Hume-Rothery rules. Here, pressure has made the disorder (or alloy) easier. Under pressure, there is a clear charge transfer from Bi to Te as deduced from Bader analysis [23] and as a result, the atomic radii of Bi and Te ions becomes approximately equal $(r_{\rm Bi}/r_{\rm Te} \approx 0.97$ at 20 GPa), favorable for the disorder. Note that in spite of the theoretical difficulty in simulating disordered structure, our predicted nine- or tenfold C2/m structure does have a bcc-like structural order as seen in the structure [Fig. 1(d)] and also in the overall theoretical and experimental agreement on the bcc-XRD peaks [23]. The enthalpy

calculation [Fig. 2(a)] suggests the bcc-like structure (nineor tenfold C2/m structure) is favorable above 15 GPa, in good agreement with the experimental transition pressure (~ 14.4 GPa). Note that a true disordered bcc structure could have a lower enthalpy, thus lowering the calculated transition pressure for a better agreement. We have also mimicked the random occupancy of Bi and Te ions [23] to establish the dynamic stability of this Bi-Te alloy. It is found that the energy differences between different occupancies vary from ~1.0 to less than 8.0 meV/atom. Such lowenergy variations could naturally lead to the random distribution of Bi and Te atoms on the bcc sites.

The discovered high-pressure polymorphs of Bi₂Te₃ invite us to reveal a rich chemistry of Bi enabling the formation of six, seven, and eight covalent bonding with Te at elevated pressures. Figure 1 shows the structure evolution with pressure, which can be viewed as a continuously monoclinic distortion. Pressure breaks the originally layered structure to form more compact structures with a larger coordination number up to eight at phase III, and eventually the compound evolves into the bcc disordered structure. The basic building blocks for phases I-III are closely related to different kinds of polyhedrons centered by Bi and apex by Te. As the pressure increases, the intralayer displacement of α -Bi₂Te₃ leads to the stabilization of BiTe₇ in β -Bi₂Te₃, where a parallel movement of $BiTe_6$ along the [110] direction is taken place [23]. On further compression, the interlayer compression of β -Bi₂Te₃ results in an involvement of extra Te to stabilize the three-dimensional γ -Bi₂Te₃ made of BiTe₈ hendecahedrons. The HP stability of bcc disordered structure is the consequence of rotation of BiTe₈.

An analysis of the densities of states [23] suggests that α -Bi₂Te₃ is a semiconductor, but HP phases are metallic. The densities of states at the Fermi level increases with elevated pressures, implying the enhanced metallicity. This is in accordance with the experimental observations [7,10–12] of HP superconductivity. We found through Bader charge analysis that the Bi \rightarrow Te charge transfers increase from 0.7468*e* to 1.1429*e* with pressure, resulting in an enhanced HP ionicity. Though the covalent bonds remain, they become weaker under higher pressure.

In summary, we have demonstrated that Bi_2Te_3 becomes magic again under high pressure with the intriguing formation of a substitutional alloy. The alloy adopts a bcc disordered structure stable at >14.4 GPa up to at least 52.1 GPa. The use of advanced theoretical techniques via a PSO algorithm on crystal structure prediction allows us to correctly predict the HP phases II and III as seven- and eight-fold monoclinic structures, respectively, followed by the confirmation of fine Rietveld refinements on experimental XRD data. This work represents a significant step forward in understanding the HP phase diagram of Bi_2Te_3 , and also provides a novel way to search for alloys. Subsequent HP synthesis of other alloys might be anticipated to greatly increase the choice of materials for a variety of applications.

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Note added in proof.—After our manuscript was accepted for publication we noticed a recent work [24] that reported a similar result of the bcc disordered structure in Bi_2Te_3 .

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