High-pressure structures of InBi predicted by particle swarm optimization algorithm*

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We extensively explore the high-pressure structures of InBi by using a newly developed particle swarm optimization algorithm. An orthorhombic *Imma* structure is discovered to be stable from 43.7 GPa to 107.9 GPa, ruling out the previously speculated cubic structure. Further increasing the pressure, we find a tetragonal $P4/nmm$ structure which is energetically more favourable from 107.9 GPa to 200 GPa. Especially, the tetragonal $P4/nmm$ structure is known to occur at high pressure in the structures of ZnO and MgTe. We also predict this structure to be a high-pressure structure of ZnTe. Thus the tetragonal $P4/nmm$ structure may be a universal high-pressure structure of the II–VI and the III–V compounds.

Keywords: InBi, structure prediction phase transitions

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1. Introduction

High pressure behaviour of substance is of great importance to materials science. Pressure could effectively shorten the interatomic distance in material and significantly change the electronic bonding state to modify the physical properties. Recent studies show that simple substance and compound exhibit anomalous properties under compression, e.g. superhard,[1−3] superconductivity,[4−9] elemental dissociation,[10,11] and metal-to-semiconductor transition.[12,13] The underlying effects can exist in other elements and compounds under sufficient compression. Group III–V binary compounds have been intensively studied experimentally and theoretically due to their extensive applications in industry and rich structural phase transitions under pressure.[14−21] InBi, as a metallic III–V compound which crystallizes into a tetragonal structure rather than a common cubic structure common for semiconducting III–V compound has attracted great attention.

InBi crystallizes in ambient condition into the tetragonal $tP4$ structure with $c/a = 0.95$ (space group: $P4/nmm$).[22] Degtyareva *et al.*[23] have reported that under compression the initial tetragonal $tP4$ structure transforms to another $tP4$ β-Np-like structure with $c/a = 0.65$ ($P4/nmm$) at about 7 GPa and further to a compositionally disordered tetragonal body-centered structure $tI2$ ($P4/mmm$) at about 20 GPa. At higher pressures (55 GPa–75 GPa), some new X-ray diffraction lines in addition to phase III were observed, which was speculated to be the hints of a new cubic body-centered $cI2$ structure. Due to the complex valence electrons assignments of indium and bismuth elements require enormous computation time. There are reported few theoretical studies on InBi under high pressure. And there is a possibility that the hitherto unsuspected structures at higher pressure are difficult to observe experimentally. It is necessary to use an effective method to search for the high pressure structures of InBi. The recent great development of crystal structure prediction through particle swarm optimization (PSO) technique[24] has made possible the blind prediction of crystal structures with the only known information about chemical compositions. The PSO technique has been implemented in CALYPSO code[25] and successfully applied to high pressure phase transitions.[26−30] Here, we extensively explore the high-pressure phases of InBi by using the PSO algorithm for crystal structure prediction. We rule out the earlier proposed $cI2$ structure. Two new high pressure structures are first reported here for InBi: an orthorhombic *Imma* and a tetragonal $P4/nmm$ structures.

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2. Methods

Structure searches for InBi were performed with the global minimization of free energy surfaces merging *ab initio* total-energy calculations via the PSO technique as implemented in CALYPSO. The underlying *ab initio* structure relaxations were performed using the density functional theory (DFT) within the generalized gradient approximation (GGA)[31] as implemented in the Vienna *ab initio* simulation package (VASP) code.[32] The all-electron projector-augmented wave (PAW) method[33] was adopted with the choices of $4d^{10}5s^25p^1$ valence electrons for In atom and $5d^{10}6s^26p^3$ valence electrons for Bi atom. The cutoff energy (450 eV) for the expansion of the wave function into plane waves and proper Monkhorst–Pack [34] k meshes were chosen to ensure that all structures were well converged to better than 1 meV/atom. The phonon calculations were carried out by using a supercell[35] approach as implemented in the PHONONPY code.[36]

3. Results and discussion

Structure predictions were performed with 2 f.u. and 4 f.u. (per simulation cell) at 10, 80 and 150 GPa, respectively. Earlier proposed tetragonal $tP4$ structure and tetragonal body-centered $tI2$ structure are successfully reproduced in the current simulation. It gives us confidence to further explore the ultrahigh-pressure phases of InBi. At 80 GPa, we obtain the orthorhombic *Imma* structure (4 f.u./unit cell) which is most energetically favourable as shown in Fig. 1(a). Both three In atoms and three Bi atoms form an isosceles triangle with the bottom parallel to a axis. The *Imma* structure can be seen as the triangle with Bi and the triangle with In alternately piled up in the direction perpendicular to c axis. It has the optimized lattice parameters: $a = 3.202$ Å (1 Å=0.1 nm), $b = 4.691$ Å, and $c = 9.418$ Å, with In and Bi atoms occupying four equivalent Wyckoff 4e positions: (0, 0.25, 0.634) and (0, 0.25, 0.116). With the pressure increasing up to 150 GPa, our simulations uncovered a tetragonal $P4/nmm$ structure (2 f.u./unit cell) becomes most preferable as shown in Fig. 1(b). In this structure, the chain of two In (Bi) atoms which is parallel to a axis and another chain parallel to c axis form a distorted tetrahedron. The $P4/nmm$ structures can be seen as two kinds of tetrahedrons alternately piled up in the direction perpendicular to c axis. It has the optimized lattice parameters: $a = 3.092$ Å, $b = 3.092$ Å and $c = 6.356$ Å, with In and Bi atoms occupying two equivalent Wyckoff 2c positions: (0, 0.5, 0.611) and (0, 0.5, 0.138). Moreover, we also uncover the previous proposed cubic Pm-3m (B2) structure[23] within the simulations at both pressures.

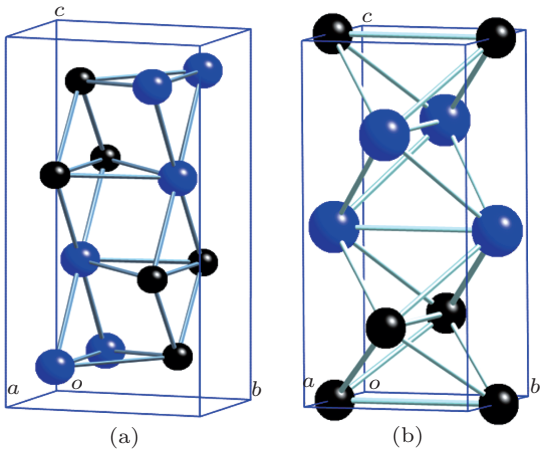


Fig. 1. (colour online) Crystal structures of the predicted orthorhombic (a) *Imma* and tetragonal (b) $P4/nmm$ phases. The large blue and small black spheres represent Bi and In atoms, respectively.

The enthalpy curves each as a function of pressure for various structures relative to $tI2$ ($P4/mmm$) structure were calculated at zero temperature, which are shown in Fig. 2. It is clear that our results correctly explore the experimental phase transition sequence (I → II→ III).[23] Compared with the earlier structures, our predicted *Imma* structure is most stable up to around 43.7 GPa, beyond which tetragonal $P4/nmm$ structure becomes most favourable. The

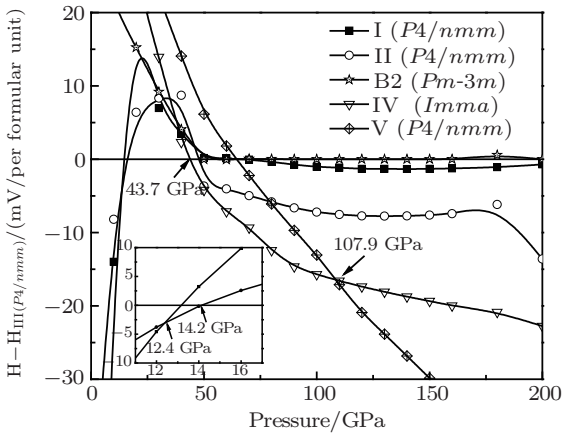


Fig. 2. Enthalpy differences relative to III ($P4/mmm$) phase each as a function of pressure for I ($P4/nmm$), II ($P4/nmm$), B2 (Pm-3m), IV (*Imma*), V ($P4/nmm$) phases. The inset clearly shows the I → II→ III transition sequence.

previously proposed cubic Pm-3m (B2) structure has poor thermodynamic stability, which can be found

from the enthalpy curves. Phonon calculations give a criterion for the crystal stability and indicate, through soft modes, structural instability.[37] Therefore, we calculated phonon dispersion curves for the *Imma* and $P4/nmm$ structures as shown in Fig. 3. Our phonon calculations at 60 GPa and 120 GPa have verified that *Imma* and $P4/nmm$ structures are dynamically stable by demonstrating the absence of any imaginary phonon frequency in the whole Brillouin zone.

The equation of state (EOS) is calculated together with the experimental data[23] (see Fig. 4). It is found that the calculated EOSs accord well with the experimental data. Especially, the EOSs of phase IV (*Imma*) are in excellent agreement with the experimental results in a pressure range of 43 GPa to 75 GPa. The III → IV phase transition is weak first order within a volume drop less than 1%, which is also in accordance with the experimental results (less than 1%). In order to understand the electronic properties, the total and the partial DOSs of phase IV (*Imma*) at 60 GPa and phase V ($P4/nmm$) at 120 GPa as shown in Fig. 5. Both phases show metallic behaviours by the evidence of the finite electronic DOS at the Fermi level. From the partial DOS, it reveals that the electrons contributing to Fermi surface are mainly from p electrons of Bi and In.

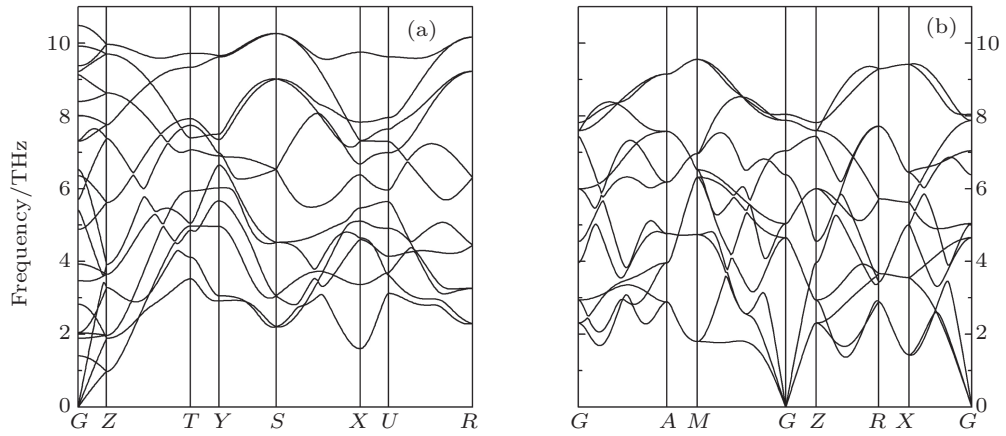


Fig. 3. Phonon dispersion curves of *Imma* (a) and $P4/nmm$ (b) structures of InBi, calculated at 60 GPa and 120 GPa, respectively.

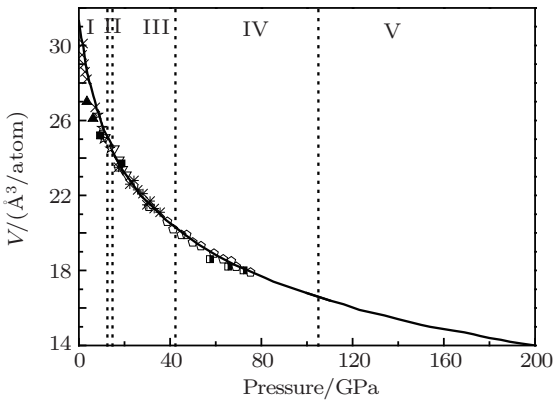


Fig. 4. The calculated equation of states (EOS) (solid line) compared with the experimental data (symbols) from Ref. [23]. Crosses: phase I, triangles: phase II, circles: phase III, squares: phase IV. Open symbols denote compression and solid symbols decompression, respectively.

It is very interesting that Li *et al.*[38] found that many of the AB-type binary compounds under high pressure will undergo orthorhombic structure. Moreover, recent studies show that ZnO and MgTe each present the tetragonal $P4/nmm$ structure at higher pressure.[39,40] We also predicted the tetragonal $P4/nmm$ structure as a high pressure phase of ZnTe. Enthalpy calculation reveals that this phase is stable above 81 GPa after the *Cmcm* phase, which is in good agreement with the experimental results of 85 GPa.[41] Since the orthorhombic $P4/nmm$ structure is a common high pressure phase of II–VI and III–V compounds, we speculate that these structures are universal high-pressure phases of the II–VI and the III–V compounds.

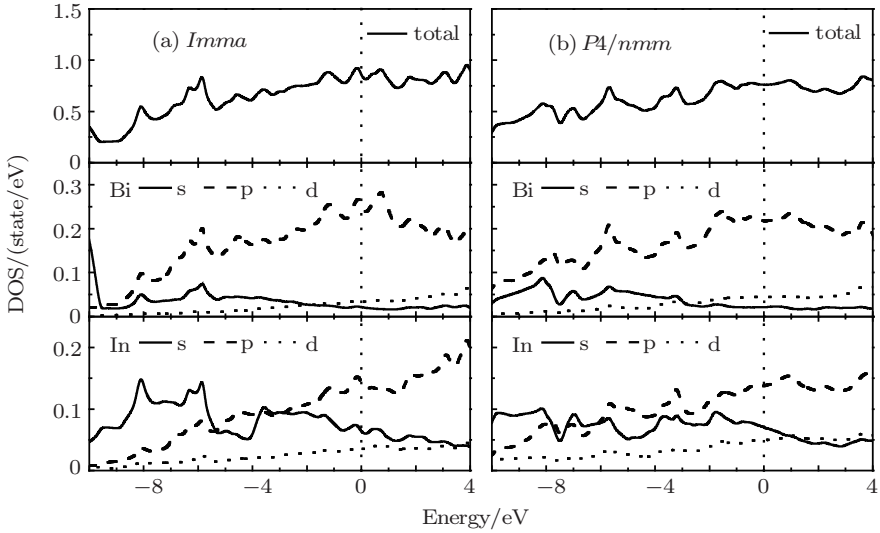


Fig. 5. The calculated densities of states (DOSs) of InBi, the vertical dot line indicates the Fermi level.

4. Conclusions

We extensively explored the high-pressure crystal structures of InBi by using a newly developed particle swarm optimization (PSO) algorithm for crystal structure prediction, We reported, for the first time, on an orthorhombic *Imma* structure as the fourth high pressure phase of InBi, which is more stable than the previously proposed cubic structure. We first predicted a tetragonal $P4/nmm$ structure as the fifth high-pressure phase of InBi. Phonon calculations revealed that the two simulated structures are dynamic stable. The orthorhombic and the tetragonal $P4/nmm$ structures may be universal high-pressure phases of the II–VI and the III–V compounds.

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