

# Structure solution in binary systems under high pressure: phase decomposition and phase synthesis

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There are binary systems (compounds) for which no structural solution can be found for a new high-pressure state by assuming a single phase. In accordance with Gibb's phase rule, an additional variable – composition – leads to an additional degree of freedom for a binary system (one more than in a one-component system). Although the bulk composition of a system may remain fixed, compositional variation between phases should be taken into account when considering phase transitions under pressure in binary compounds. This approach allows for a binary system the following kinds of phase transitions that are not possible in a one-component system: (i) phase (compound) decomposition into two phases with different compositions; (ii) phase synthesis from two initial phases; and (iii) phase separation from an initial phase into phases of different compositions. Examples of these kinds of high-pressure transformations and structure solution are given for the following binary systems: In–Bi, In–Sn, Hg–Sn, Cd–Sb and Sn–Bi.

## 1. Introduction

Structural studies at high pressure are focused mainly on elements or compounds that are also stable under ambient conditions. Compounds are usually considered as quasi-one-component systems, implying that structural transitions in such systems occur without any change in composition. However, a binary (multicomponent) compound is just a particular state of a binary (multicomponent) system, stable at a certain stoichiometric composition under normal  $P$ – $T$  conditions. In general, the composition in a binary system is a variable parameter along with pressure and temperature. This fact should be taken into account if considering phase transitions under pressure in binary alloy systems or compounds. Systematic studies on binary alloy systems have been performed at the Institute of Solid State Physics, Chernogolovka, Russia (e.g. Ponyatovskii & Degtyareva, 1989). These studies provided examples of compound decomposition and new phase synthesis under high pressure–temperature conditions. Our further studies on binary compounds at extended ranges of pressures and temperatures raise the following questions: to what extent should binary (multicomponent) phases or compounds be considered quasi-one-component systems, and do the phase transitions occur without a change in composition as simple polymorphic transitions?

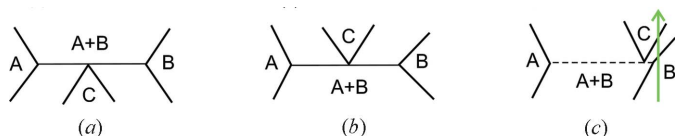
Consideration of the composition as a variable for binary phases and compounds is important for interpreting phase

transitions at high pressure and high temperature because diffusion rates may be sufficient to attain the equilibrium state. High-pressure experiments at ambient temperature may result in a metastable state of a binary phase/compound because of kinetic hindrance and lower diffusion rates.

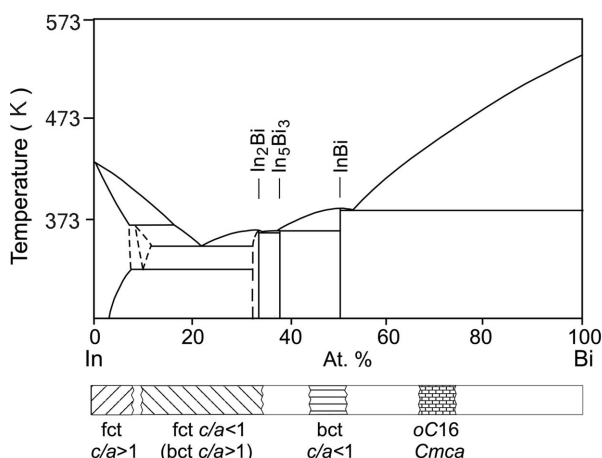
## 2. Methodology

According to Gibb's phase rule, the number of degrees of freedom ( $f$ ) for a multicomponent system under hydrostatic pressure is  $f = k + 2 - p$ , where  $p$  is a number of phases coexisting in equilibrium,  $k$  is the number of components and '2' denotes two thermodynamic variables, pressure and temperature. For a two-component system ( $k = 2$ ) with one variable (e.g. pressure), the number of coexisting phases can be up to  $p = k + 1 = 3$ , if  $f = 0$  (at a certain point on a phase diagram). Possible cases of phase equilibrium for  $k = 2$  are shown schematically in Fig. 1, illustrating the coexistence of three phases.

If the variable pressure or temperature is changed (vertical axis), an intermediate phase ( $C$ ) can decompose into  $A + B$  phases of different compositions (horizontal axis), as shown in Fig. 1(a). An intermediate phase synthesis is shown in Fig. 1(b). A particular case where a new phase forms at the expense of an initial phase is illustrated in Fig. 1(c) (called phase separation).


**Figure 1**

Examples of phase equilibrium in a binary system: (a) decomposition of an intermediate phase  $C \rightarrow A + B$ ; (b) formation of a new intermediate phase  $A + B \rightarrow C$ ; (c) phase separation from the initial phase with a change in composition  $B \rightarrow C + B$ . The horizontal axis is composition; the vertical axis is temperature or pressure.


**Figure 2**

The In–Bi phase diagram. (Upper plot) Ambient pressure: stoichiometric compounds  $\text{In}_2\text{Bi}$ ,  $\text{In}_5\text{Bi}_3$  and  $\text{InBi}$ . (Lower plot) High pressure,  $\sim 10$ – $20$  GPa: phase sequence  $\text{fct } c/a > 1 \Rightarrow \text{fct } c/a < 1 \Rightarrow \text{bct } c/a < 1 \Rightarrow \text{Cmca}$  (see text).

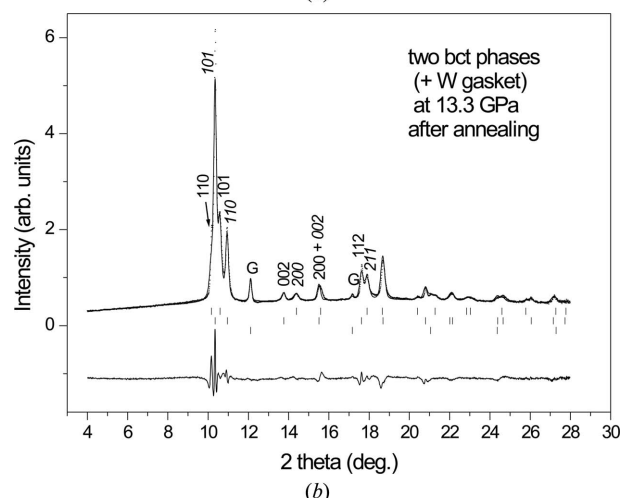
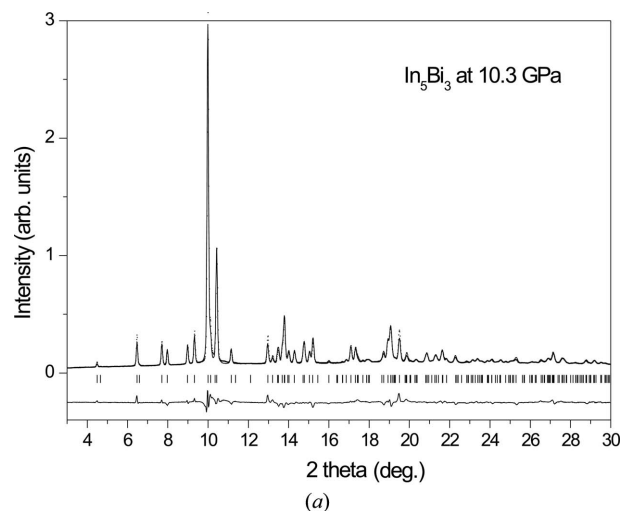
### 3. Compound decomposition

#### 3.1. The In–Bi system

The In–Bi alloy system (Massalsky, 1996; Pearson, 1967) has three intermediate compounds at ambient pressure:  $\text{In}_2\text{Bi}$ ,  $\text{In}_5\text{Bi}_3$  and  $\text{InBi}$ , as shown in Fig. 2. These compounds are stable at certain stoichiometric compositions and have crystal structures of a site-ordered type.

$\text{InBi}$  was studied by energy-dispersive diffraction with synchrotron radiation in a diamond-anvil cell under pressure up to 75 GPa (Degtyareva *et al.*, 1998). The initial tetragonal structure,  $tP4$ , space group  $P4/nmm$ , with  $c/a = 0.95$ , first transforms with a strong compression along the  $c$  axis to a similar tetragonal structure with  $c/a = 0.65$  and then, at a higher pressure, to a tetragonal body-centered structure,  $bct$ , of a random (site-disordered) type. The  $bct$  phase shows an increase in  $c/a$  from 0.91 to 0.96 in the pressure range from 20 to  $\sim 70$  GPa. Some evidence was obtained for a transition to a cubic body-centered structure,  $bcc$ , at around 70 GPa.

$\text{In}_5\text{Bi}_3$  crystallizes in a tetragonal structure with lattice parameters  $a = 8.544 \text{ \AA}$  and  $c = 12.68 \text{ \AA}$ , 32 atoms in the unit cell, and space group  $I4/mcm$ . Recent studies under pressure have shown that this structure remains stable at least up to 25 GPa (Degtyareva & Degtyareva, 2002). However, after annealing the  $\text{In}_5\text{Bi}_3$  sample at 15 GPa and 423 K for 4 h, the diffraction pattern changes and reveals a phase transition (see Fig. 3). No solution for this pattern was found by assuming this


**Figure 3**

Angle-dispersive diffraction patterns (integrated profiles) from  $\text{In}_5\text{Bi}_3$  (a) at 10.3 GPa without heating and (b) at 15 GPa after annealing at 423 K for 4 h, corresponding to a decomposition in a two-phase mixture with  $bct \ c/a < 1$  and  $bct \ c/a > 1$ . Rietveld refinements of the diffraction patterns are shown. ‘G’ denotes peaks from the gasket material.  $\lambda = 0.4654 \text{ \AA}$ . For experimental details see Degtyareva & Degtyareva (2002).

state to be a single-phase state. However, a solution was found by assuming a two-phase mixture, where the two phases are both body-centered tetragonal, space group  $I4/mmm$ , but differ in axial ratios. One phase with the axial ratio  $c/a = 0.92$  is assigned as  $bct \ c/a < 1$ , and the other phase with  $c/a = 1.13$  is assigned as  $bct \ c/a > 1$  (see Table 1). The atomic volumes of the two phases are slightly different, which allowed us to estimate with the help of Vegard’s law the difference in their compositions (about 10 at.%). This observation implies that  $\text{In}_5\text{Bi}_3$  decomposes into two phases of different compositions; one is above and one is below the initial  $\text{In}_5\text{Bi}_3$  composition. This transformation is reversible, and the  $\text{In}_5\text{Bi}_3$  compound is recovered on decompression.

In the Bi-rich region of the In–Bi alloy system, a complex phase was found near the composition  $\text{In}_{30}\text{Bi}_{70}$  with the crystal structure determined recently as  $\text{Cmca-oC16}$  (Degtyareva, 2000). The stability region of the  $\text{Cmca-oC16}$  phase seems to extend in composition on the  $T$ – $P$ – $x$  diagram up to pure Bi,

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because Bi-IV is reported to have the same  $Cmca-oC16$  structure (Degtyareva, 2000).

Under high pressure, a sequence of metallic site-disordered phases can be outlined, with extended regions of stability, as shown schematically in the lower plot of Fig. 2. The structures of the phases in this sequence are determined by the number of valence electrons per atom, as in so-called Hume–Rothery phases. The In-rich region of the In–Bi alloy system displays the following structural sequence under high pressure:

$$fct\ c/a > 1 \Rightarrow fct\ c/a < 1 (= bct\ c/a > 1) \Rightarrow bct\ c/a < 1.$$

This sequence is consistent with that for the In–Sn alloy system at ambient and high pressure, as discussed below.

There is much similarity in the high-pressure phases of binary alloys and high-pressure forms of group IV elements. This fact implies that these phases are common representatives of polyvalent  $sp$  metals and alloys, rather than particular

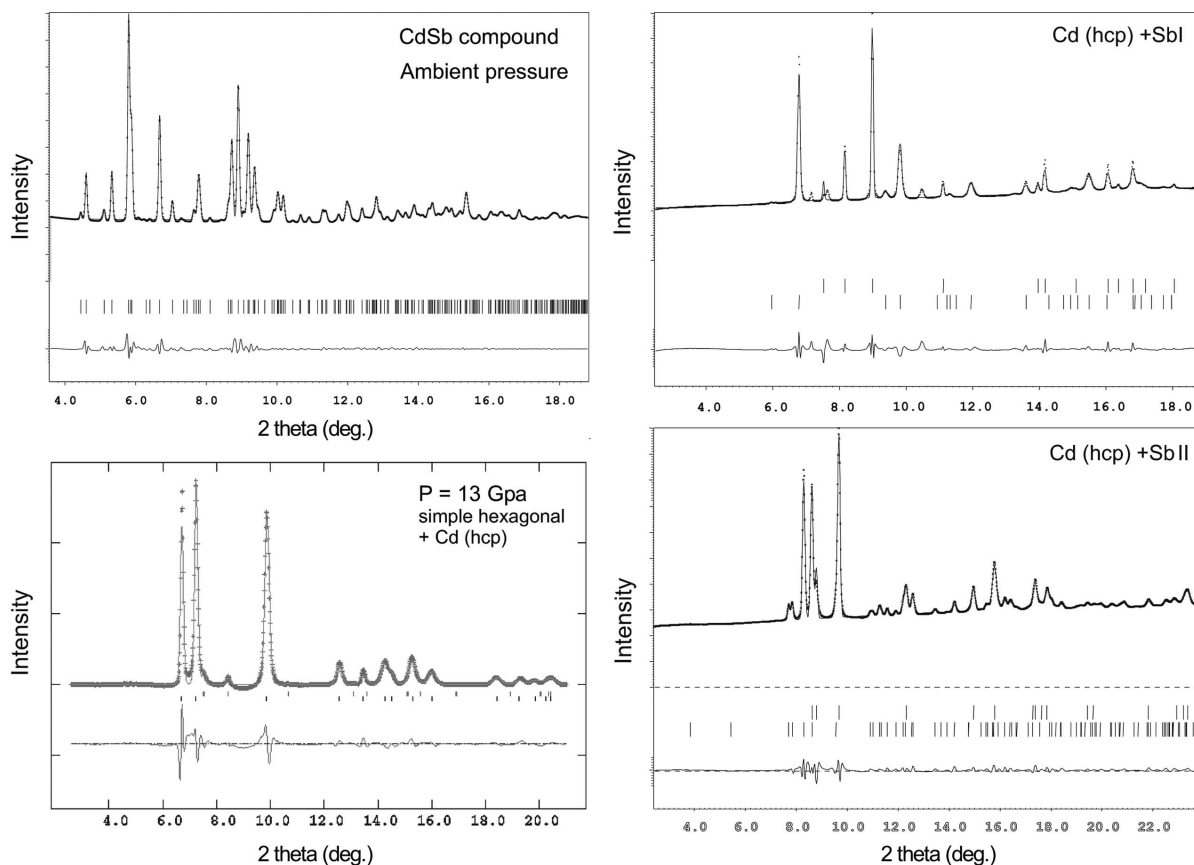
characteristics of a certain element or a group of the periodic table.

## 3.2. The Cd–Sb system

The Cd–Sb alloy system has, at ambient pressure, one intermediate compound of equiatomic composition, CdSb, which is orthorhombic, space group  $Pbca$ , with 16 atoms in the unit cell (Pearson symbol  $oP16$ ). The refined lattice parameters from our sample under ambient conditions give  $a = 6.473\ \text{\AA}$ ,  $b = 8.248\ \text{\AA}$  and  $c = 8.531\ \text{\AA}$ , which are very close to the values given by Pearson (1967). High-pressure studies showed (Degtyareva *et al.*, 2005) that the CdSb compound becomes unstable above 7 GPa, and a new phase forms with the simple hexagonal ( $sh$ ) structure,  $hP1$ , space group  $P6/mmm$ , with Cd and Sb randomly occupying the atomic sites. In addition to the  $sh$  phase, some weak diffraction peaks were observed showing an excess of Cd with the close-packed hexagonal ( $hcp$ ) structure. At a pressure of  $P = 13\ \text{GPa}$ , the lattice parameters for the  $sh$  phase are  $a = 3.025\ \text{\AA}$  and  $c = 2.829\ \text{\AA}$ , and for  $hcp$ -Cd  $a = 2.904\ \text{\AA}$  and  $c = 5.045\ \text{\AA}$ .

**Table 1**  
Structural characteristics of phases in the  $\text{In}_5\text{Bi}_3$  alloy at 15 GPa after annealing at 423 K.

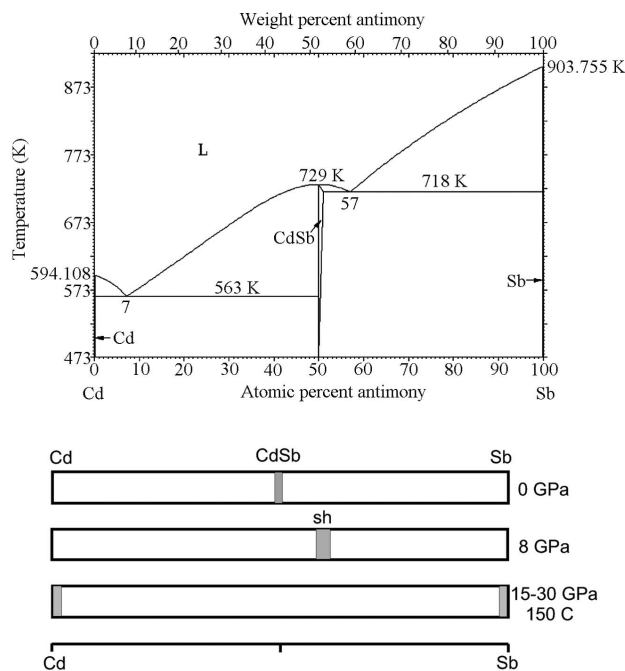
Phase	$a$ (Å)	$c$ (Å)	$c/a$ ( $bct$ )	$V_{at}$ (Å <sup>3</sup> )	Composition (at.% Bi)	Electron concentration (electrons per atom)
$bct\ c/a < 1$	3.715 (3)	3.426 (7)	0.923 (2)	23.67 (6)	~44	3.88
$bct\ c/a > 1$	3.447 (2)	3.883 (3)	1.126 (1)	23.07 (3)	~34	3.68



**Figure 4**  
Diffraction patterns of CdSb, illustrating compound decomposition. (Left, upper panel) Ambient pressure: initial CdSb compound; (left, lower panel)  $P = 13\ \text{GPa}$ : simple hexagonal phase and pure Cd ( $hcp$ ) ( $\lambda = 0.3311\ \text{\AA}$ ). (Right, lower panel) 30 GPa: further decomposition into nearly pure Cd ( $hcp$ ) and SbII (host–guest) phases after annealing at  $\sim 20\ \text{GPa}$  and 423 K for 3 h; (right, upper panel) ambient pressure, on decompression: Cd ( $hcp$ ) and SbI ( $\lambda = 0.3675\ \text{\AA}$ ). Integrated spectra and Rietveld refinements are shown.

Further pressure increases and annealing under 15–25 GPa at 423 K for 3 h disproportionated the sample into nearly pure Cd and Sb. The refined lattice parameters at 30 GPa are, for *hcp*-Cd,  $a = 2.824(1) \text{ \AA}$ ,  $c = 4.796(1) \text{ \AA}$ ,  $cla = 1.698$  and  $V_{\text{at}} = 16.56 \text{ \AA}^3$ , and for SbII (tetragonal host–guest structure),  $a_{\text{H}} = 7.738(1) \text{ \AA}$ ,  $c_{\text{H}} = 3.741(1) \text{ \AA}$ ,  $c_{\text{G}} = 2.862(1) \text{ \AA}$ ,  $c_{\text{H}}/c_{\text{G}} = 1.3067$ ,  $V_{\text{at}} = 21.105 \text{ \AA}^3$  and  $V/V_0 = 0.699$ , as in pure Sb (Degtyareva *et al.*, 2004). On decompression, the sample remained nearly pure Sb and Cd. The refined lattice parameters at ambient pressure are, for *hcp*-Cd,  $a = 2.982(1) \text{ \AA}$ ,  $c = 5.599(1) \text{ \AA}$ ,  $cla = 1.878$  and  $V_{\text{at}} = 21.56 \text{ \AA}^3$  (for pure Cd,  $a = 2.9788 \text{ \AA}$ ,  $c = 5.6164 \text{ \AA}$ ,  $cla = 1.885$  and  $V_{\text{at}} = 21.58 \text{ \AA}^3$ ); for SbI,  $a = 4.294(1) \text{ \AA}$ ,  $c = 11.283(1) \text{ \AA}$ ,  $cla = 2.628$  and  $V_{\text{at}} = 30.02 \text{ \AA}^3$  [for pure Sb,  $a = 4.308 \text{ \AA}$ ,  $c = 11.274(1) \text{ \AA}$ ,  $cla = 2.617$  and  $V_{\text{at}} = 30.20 \text{ \AA}^3$ ]. The corresponding diffraction patterns are shown in Fig. 4.

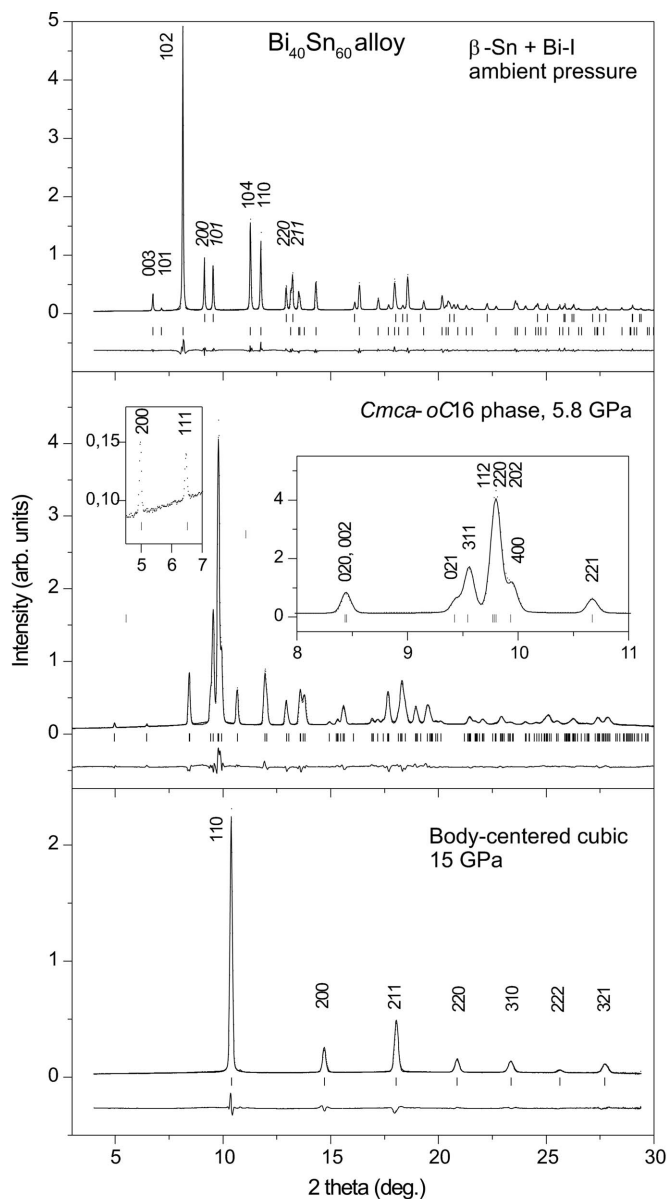
The observed phase transitions of the CdSb compound upon increasing pressure reveal two stages of decomposition: (i) formation of the *sh* phase of composition  $\sim 55\text{--}60 \text{ at.}\%$  Sb with an excess of Cd; (ii) disproportionation of the sample into nearly pure components Cd and Sb, as shown in Fig. 5. The decomposition of CdSb is confirmed by phase transitions on decompression. There was no reversible transformation to the initial compound at ambient pressure: after (i) an amorphous phase was obtained and after (ii) a phase mixture of Cd and SbI was recovered. It should be noted that the high-pressure intermediate phase in the Cd–Sb system has the simple hexagonal structure, the same as ambient-pressure intermediate phases in the In–Sn and Hg–Sn systems discussed below (§5).



**Figure 5**  
(Upper panel) Temperature–composition phase diagram of the Cd–Sb system at normal pressure (Massalsky, 1996). Lower panels represent phases along composition at ambient and high pressures, illustrating two stages of compound decomposition:  $\text{CdSb} \rightarrow \text{sh} + \text{Cd} \rightarrow \text{SbII} + \text{Cd}$ .

#### 4. New phase synthesis

The Sn–Bi alloy system is of a simple eutectic type. An intermediate SnBi phase formation under pressure was first reported by Bridgman (1964). Recent high-pressure studies on the SnBi alloy yielded a structure solution for the high-pressure phase (Degtyareva *et al.*, 2003). Fig. 6 shows diffraction patterns of the SnBi alloy at ambient and at high pressure, illustrating phase transitions from the initial two-phase mixture  $\beta\text{-Sn} + \text{Bi}$  to an intermediate phase of site-ordered type and further transition to a new intermediate phase of site-disordered type. The high-pressure SnBi phase is formed after annealing the sample at 2.9 GPa and 423 K for 1 h. The pattern at 5.8 GPa was fitted with an orthorhombic *Cmca*–



**Figure 6**  
Diffraction patterns from the SnBi alloy and Rietveld refinement fits. (Upper) Ambient pressure:  $\beta\text{-Sn} + \text{Bi-I}$ . (Middle) 5.8 GPa: the *Cmca*–*oC16* phase, (partially) site-ordered. The insets show expanded views of the two low-angle peaks and of the first group of strong reflections. (Lower) 15 GPa: body-centered cubic phase, site-disordered.

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*oC16* structure with lattice parameters  $a = 10.7345$  (5) Å,  $b = 6.3270$  (7) Å and  $c = 6.3115$  (8) Å. The atomic positions are determined as *8f*:  $x = 0$ ,  $y = 0.1670$  (1) and  $z = 0.3337$  (1) with 85% Sn and 15% Bi, and *8d*:  $x = 0.2124$  (1),  $y = 0$ ,  $z = 0$  with 35% Sn and 65% Bi. The next transition, at pressures above 12 GPa, occurs to a phase with a body-centered structure, which is completely site-disordered. No ‘superstructure’ reflections were observed in the diffraction pattern recorded at 15 GPa (Fig. 6, lower panel) which was fitted with a *bcc* structure,  $a = 3.6336$  (1) Å.

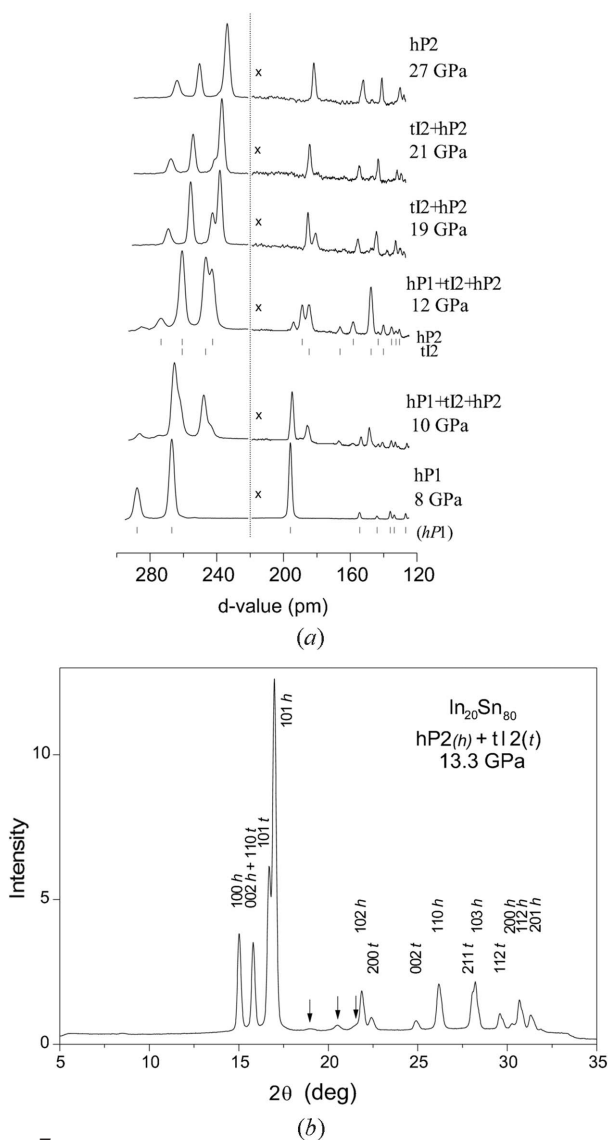
Similar intermediate phases with *Cmca-oC16* structure formed under pressure in the In–Bi and Pb–Bi alloy systems as well as in pure Bi (Degtyareva, 2000). This type of structure was previously reported for the high-pressure modification of group IV elements Si and Ge (Hanfland *et al.*, 1999; Takemura *et al.*, 2000). One can conclude that the *Cmca-oC16* structure is

typical for high-pressure phases of *sp* metals in the range of valence electrons from 4 to 5. Comparison of all the *Cmca-oC16* structures indicates a clear similarity in the observed axial ratios  $b \simeq c \simeq a/3^{1/2}$  and atomic positions  $y$  (*8f*)  $\simeq 1/6$  and  $z$  (*8f*)  $\simeq 1/3$ . This result implies the importance of these particular values for the stability of the structure.

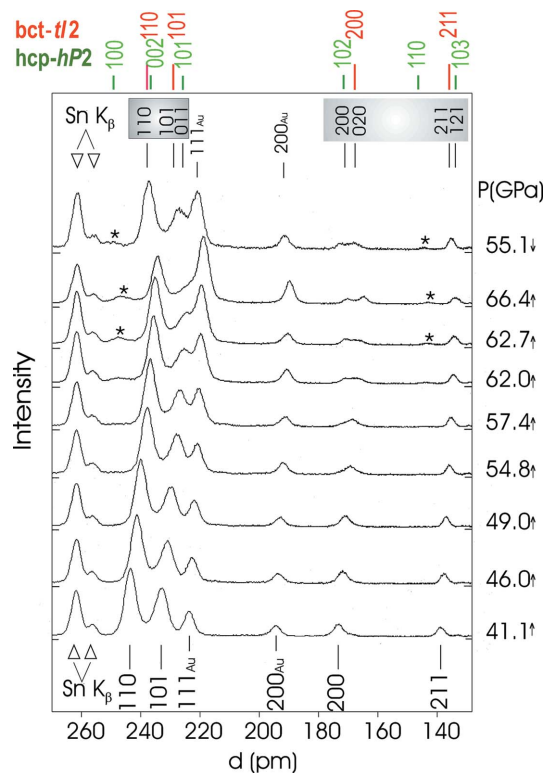
Observation of the *bcc* structure in the SnBi alloy above 12 GPa suggests that *bcc* structures are stable in a wide composition range from Sn, where *bcc* exists above 40 GPa, to Bi, where *bcc* is formed at 8 GPa (Young, 1987).

## 5. Phase separation

The phase transition shown in Fig. 1(c) occurs in the In–Sn and Hg–Sn alloy systems under pressure (Degtyareva *et al.*, 1999, 2000). Both initial alloys have simple hexagonal phases, *hP1*, space group *P6/mmm*, corresponding to compositions of Sn with 20 at.% In and 10 at.% Hg, respectively (Pearson, 1967). The *sh-hP1* phases in both alloys are stable to ~10 GPa and transform at higher pressures into new states. Diffraction patterns of the In<sub>20</sub>Sn<sub>80</sub> alloy gradually change in intensity, suggesting a change in the relative phase amount in a two-phase mixture (Fig. 7). A diffraction pattern of this alloy at



**Figure 7** (a) In<sub>20</sub>Sn<sub>80</sub> spectra taken on pressure increase. (b) Two-phase mixture of close-packed hexagonal (*hP2*) and body-centered tetragonal (*tI2*) phases at 13.3 GPa. Arrows denote diffraction peaks from the gasket material (spring steel with the close-packed hexagonal structure).



**Figure 8** The effect of pressure on Hg<sub>10</sub>Sn<sub>90</sub> (Degtyareva *et al.*, 1999). Au is the pressure marker. Diffraction peaks in EDXD spectra ( $2\theta = 9.52^\circ$ ) are fitted to the *tI2* structure, indexing is given for the lower pattern at 41.1 GPa. Additional diffraction peaks observed above ~55 GPa have been interpreted as orthorhombic distortion; indexing is given for the upper pattern (shaded). In the light of later results on the In–Sn system, a two-phase mixture of *bct-tI2* and *hcp-hP2* is suggested; re-indexing is given in the upper panel. This assumption explains all diffraction peaks including previously unexplained ones (marked by asterisks).

13.3 GPa was fitted with two phases,  $tI2 + hcp$ . With increasing pressure, the amount of the  $hcp$  phase increases at the expense of the  $tI2$  phase, and above 27 GPa  $hcp$  exists as a single phase (Fig. 7).

Similar results were observed previously in the  $Hg_{10}Sn_{90}$  alloy (Degtyareva *et al.*, 1999). An attempt was made to find a solution as for a single phase, and an orthorhombic phase was suggested (Fig. 8). In light of the recent study on the  $In_{20}Sn_{80}$  alloy (Degtyareva *et al.*, 2000), the data for the  $Hg_{10}Sn_{90}$  alloy above 60 GPa are now re-indexed and fitted as a two-phase mixture  $tI2 + hcp$ . Thus, both alloy systems, In–Sn and Hg–Sn, display under pressure similar transformations  $sh \rightarrow tI2 + hcp$ , the only difference being the transition pressure;  $hcp$  phases appear at the composition of 2.75 electrons per atom above 10 and 60 GPa in In–Sn and Hg–Sn, respectively.

## 6. Conclusions

Structural studies at high-pressure on binary alloys have been extended to higher pressures and temperatures. It is necessary to take into account for a binary (multicomponent) system that the number of coexisting phases at a certain  $P$ – $T$  condition is greater than that in a one-component system and is defined by the Gibbs phase rule. Therefore, in some cases a satisfactory structural solution could not be found for a single phase. Examples of diffraction studies on binary systems demonstrate common compound decompositions and new intermediate phase syntheses. High-pressure studies at ambient temperature lead in some cases to metastable states in a binary (multicomponent) system owing to the low rate of the diffusion process. The development of high-temperature experimental techniques under high pressure allows access to

an equilibrium state in a binary system yielding phase transformations discussed in the paper.

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