Synchrotron-based x-ray-diffraction study of the intermediate-high-pressure phase in the alloy $In_{0.25}Sn_{0.75}$

S. Meenakshi, V. Vijayakumar, B. K. Godwal, and S. K. Sikka
High Pressure Physics Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India
(Received 20 April 2001; published 13 November 2001)

$In_{0.25}Sn_{0.75}$ alloy stabilized in the primitive hexagonal phase at ambient conditions is studied in a diamond anvil cell at high pressures with angle-dispersive x-ray diffraction using the synchrotron radiation at ELETTRA. The ambient primitive hexagonal phase was found to undergo a reversible transformation to a mixture of body-centered-tetragonal and hexagonal-close-packed phases above 11.6 GPa and not to the *Cmca* structure assigned in Si and Ge. The occurrence of the bct phase shows similarity to the high-pressure behavior of Sn. A transformation mechanism from the ph to hcp phase via the bct structure is also described.

DOI: 10.1103/PhysRevB.64.212104 PACS number(s): 62.50.+p, 64.70.Kb, 64.30.+t, 81.40.Vw

Introduction. The high-pressure phase diagrams of the group-IVA elements have been of considerable experimental and theoretical interest.[1–3] The simple s-p electronic configuration makes them ideal candidates for *ab initio* calculations of electronic structure and phonon frequencies under pressure,[4–6] yielding transition mechanisms, equation of state, and structural stability data. These have emerged as prototype examples of the gradual loss of covalency and metallization with concurrent increase in coordination and packing. Interest in the high-pressure phase transitions in these elements has been further stimulated by the controversy about the structure of the so-called ''intermediate phase'' in Si, stable between the primitive hexagonal (ph; $P6/mmm$, $Z=1$) phase and the hexagonal-close-packed (hcp; $P6_3/mmc$, $Z=2$) phase in the pressure range of 34–43 GPa at room temperature[2,7] and in Ge above 102 GPa.[8] This phase in Si is metallic which has a superconducting transition temperature much higher than those of the ph and hcp phases,[9] implying that it is not a mixture of ph and hcp phases as was initially suspected. Vijayakumar and Sikka,[10] with the then-available energy-dispersive x-ray diffraction (EDXRD) data, had assigned a four-atom orthorhombic cell to it in Si which was like the X phases ($a_X \simeq a_{ph}$, $b_X \simeq 2c_{ph}$, $c_X \simeq \sqrt{3}a_{ph}$) in B-group alloys found by Degtyareva and Ponyatovskii.[11] These phases (X) which are in between the ph and hcp phases are similar but not identical in different alloy systems. Duclos *et al.*[7] remeasured the diffraction pattern of the intermediate phase in Si with EDXRD with better precision and found that an eight-atom cell belonging to the X-phase ($a_{X1} \simeq 2a_X$, $b_{X1} \simeq b_X$, $c_{X1} \simeq c_X$) class fits the d-spacing data better. However, no structural details were obtained. In Ge, Duclos *et al.*[7] indexed it to a double hexagonal-close-packed (dhcp) cell. Recently, Hanfland and co-workers[12] have studied the intermediate phase of Si using high-resolution angle-dispersive synchrotron x-ray diffraction. They observed that the intermediate phase of Si at 38 GPa is orthorhombic (16 atoms/cell) with the space group *Cmca*. Structural refinement showed that Si VI is isotypic to the high-pressure phase of Cs V.[12,13] The axial ratios and atomic coordinates are nearly identical for both Si and Cs in this phase. It may be noted that the 16-atom *Cmca* structure also belongs to the family of X phases (with $a_{Cmca} \simeq 2c_{X1}$, $b_{Cmca} \simeq a_{X1}$, $c_{Cmca} \simeq a_{X1}$). Theoretical *ab initio* total energy calculations by Ahuja *et al.*[14] have confirmed the stability of the *Cmca* structure.[12] Recent high-pressure angle-dispersive x-ray diffraction (ADXRD) measurements on Ge using synchrotron radiation by Takemura *et al.*[15] have shown that the *Cmca* phase is stable until 100 GPa and there was no indication for the existence of a dhcp phase in Ge around 100 GPa. First-principles studies of the high-pressure phases of Ge by Mujica *et al.*[16] have also shown that the *Cmca* phase is stable in the pressure range 91–155 GPa.

More recently, Degtyareva[17] has determined the structure of the high-pressure intermediate phases in the Bi-rich binary alloys of Pb and In to be also orthorhombic with space group *Cmca*. Degtyareva and Ponyatovskii[11] have discussed the phase relations in B-group elemental alloys as a function of pressure and varying composition. It is observed that the structural evolution obeys a homology rule; i.e., the stability of a given sequence of structures in the phase diagram depends on the electron density. As the mean number of electrons in the alloy increases, there is a sequence of phases accompanied by a decrease in the coordination number and packing density of the structure. Phases with identical structure occur in various systems for similar values of the electron density per atomic volume.

Alloying Sn with In stabilizes the ph phase at ambient conditions.[18] These alloys which are usually referred to as γ-Sn, crystallize in the ph structure with $c/a=0.93$. In this phase the metallic atoms occupy randomly the 1(a) position of $P6/mmm$. Similar phases have been obtained in more than ten Sn-based alloys by rapid quenching from the melt. The ph phase in these alloys has an average valence electron concentration of about 3.8 electrons per atom. It is important to note that in Cs, the CsV structure occurs on completion of the $s \rightarrow d$ transfer of electrons, which is not predominant in s-p block elements.[12,13] Thus it is unlikely that the CsV structure will occur in In-stabilized Sn alloys. Degtyareva *et al.*[19] have carried out high-pressure EDXRD measurements on the alloy $Hg_{0.1}Sn_{0.9}$ using synchrotron radiation. They found that the ambient ph phase transformed at 15 GPa to a bct phase similar to the high-pressure forms of Sn.[20] A recent study on the ph alloy $In_{0.2}Sn_{0.8}$ under pressure by

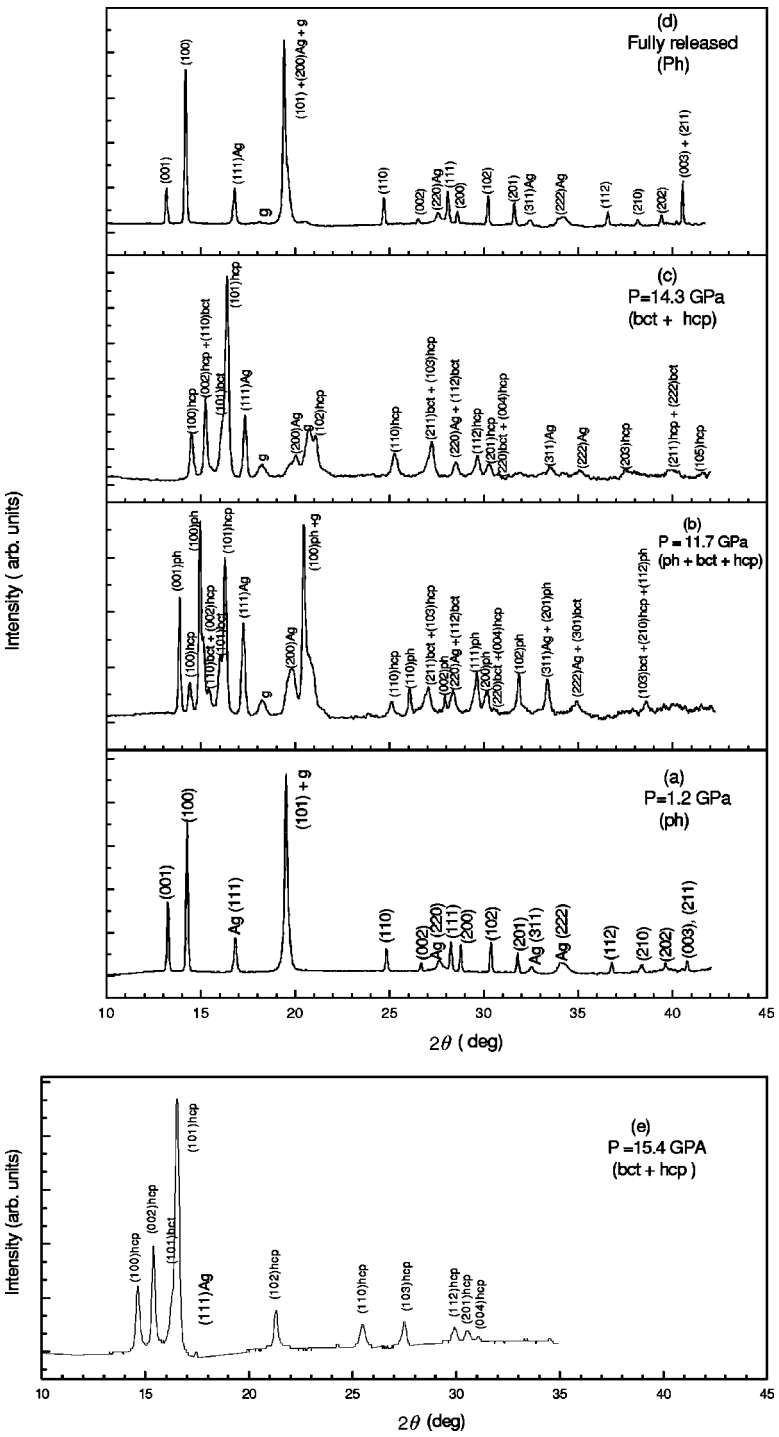

FIG. 1. (a)–(d) ADXRD patterns for $In_{0.25}Sn_{0.75}$ alloy at various pressures. (e) ADXRD pattern at 15.4 GPa under a different loading.

Degtyareva *et al.*[21] has shown that the ambient-pressure ph phase transforms above 13 GPa to a mixture of bct and hcp phases and further to a hcp phase above 23 GPa. The interesting feature here is the reversible decomposition of it into two phases that are not related to any of the known ''intermediate'' phases. However, most of these measurements were carried out using EDXRD and a few with ADXRD coupled to a rotating anode generator.

We have carried out high-pressure high-resolution ADXRD measurements using the synchrotron source at ELETTRA (Trieste, Italy) on $In_{0.25}Sn_{0.75}$ alloy formed in the ph phase at ambient conditions. The present studies were aimed at identifying possible candidates of composition-dependent intermediate phases of In-Sn. We also looked at the possibility of the *Cmca* structure observed in Si and Ge occurring in this alloy. The interest was also to obtain precise high-resolution data to study the effect of alloy concentration on structural evolution and decomposition under pressure as suggested by Degtyareva *et al.*[21] It may be noted that the stoichiometry of $In_{0.25}Sn_{0.75}$ corresponds to the AB_3-type phase. Thus in this alloy a pressure-induced and -assisted ordered phase at high pressure or consequent to a structural

transition may also occur. The aim of the present experiments was to explore such a possibility and also to investigate the path of the ph-hcp structural evolution via the intermediate phase.

Experimental details. The alloy $In_{0.25}Sn_{0.75}$ was prepared by melting together high-purity Sn and In under vacuum. The sample was characterized using x-ray diffraction at ambient conditions and was found to be in the ph phase [$a=3.214(1)$ Å, $c=2.998(1)$ Å, $c/a=0.933$, $V=26.82$ Å^3].

High-pressure angle-dispersive x-ray diffraction measurements were carried out on $In_{0.25}Sn_{0.75}$ alloy with synchrotron radiation at ELETTRA (Trieste, Italy). A modified Mao Bell diamond anvil cell[22] (DAC) was employed. A fine powder of $In_{0.25}Sn_{0.75}$ alloy along with silver as internal pressure callibrant and ethanol as pressure transmitter was loaded in a preindented stainless steel gasket. The radiation source was a 57-pole wiggler.[23] The experimental station was based on a 345 mm imaging plate (IP) area detector from MarResearch. The sample to IP distance and wavelength was calibrated using Si. The x-ray beam wavelength used was 0.68796 Å. Exposure times were about 15 min. The scanned two-dimensional diffraction patterns were corrected for tilt and scanner distortions and converted to intensity vs 2θ through radial integration using FIT2D software.[24]

Results and discussion. The evolution of the diffraction pattern at various pressures is depicted in Fig. 1. It may be noted that the ambient ph phase is retained up to 9 GPa above which new diffraction peaks appear indicating a phase transition. The diffraction patterns between 10 GPa and 14.3 GPa could not be indexed to a single phase. Various possible structures published in the literature including the orthorhombic (*Cmca*) structure proposed by Hanfland *et al.*[12] as well as the bct ($I4/mmm$) structure proposed by Degtyareva *et al.*[21] were tried for the intermediate state. The orthorhombic (*Cmca*) structure did not give a good fit in axial ratio, intensity, space group, and indexing. A better fit was obtained

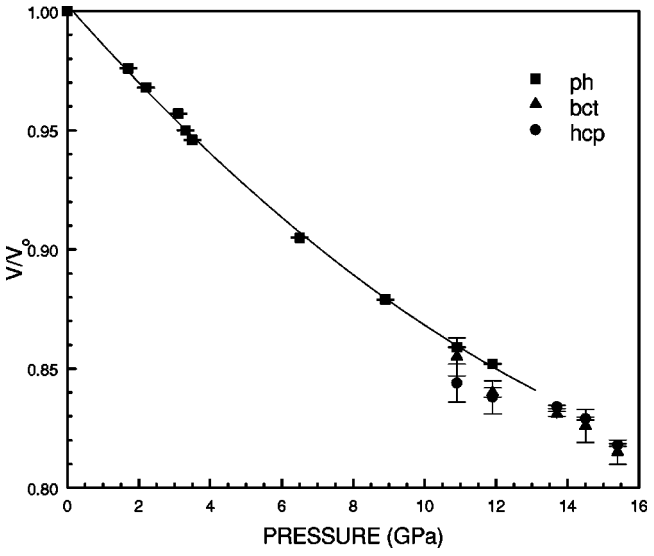

FIG. 2. Pressure-volume curve for $In_{0.25}Sn_{0.75}$ alloy. Also shown are the error bars for V/V_0.

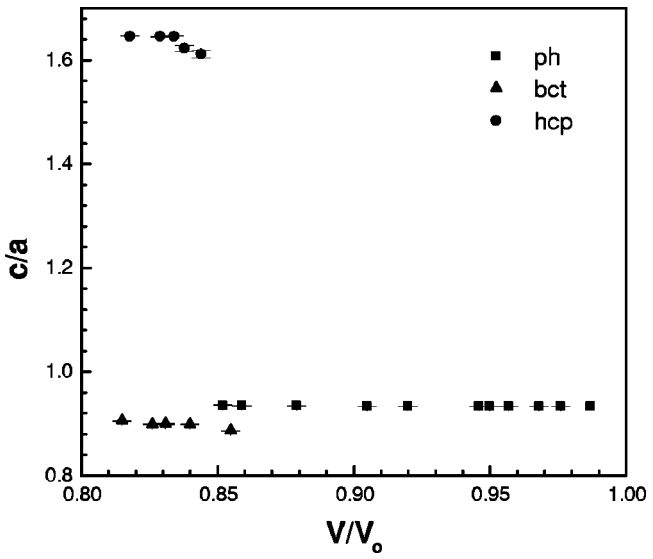

FIG. 3. Axial ratio for the ph, bct, and hcp phases as a function of V/V_0.

using a mixture of ph ($P6/mmm$), bct ($I4/mmm$), and hcp ($P6_3/mmc$) structures. This is consistent with the observation of Degtyareva *et al.*[19] that many binary alloys with valence electron concentration close to 4 should follow a structural sequence under pressure which include an intermediate bct phase as seen in $Hg_{0.1}Sn_{0.9}$ alloy where the valence electron concentration is 3.8. It has also been shown by Degtyareva[17] that the range of stability of the orthorhombic *Cmca* structure extends from four to five valence electrons. This further rules out the possibility of the occurrence of the *Cmca* structure in $In_{0.25}Sn_{0.75}$ binary alloy where the average number of valence electron is 3.75 electrons per atom and is consistent with our findings. The patterns above 10 GPa showed peaks belonging to the ph and bct as well hcp phases. Beyond 13.6 GPa, the ph phase was not observed and the diffraction pattern belonged to the bct and hcp

TABLE I. Observed d values and intensities at 14.5 GPa compared with the d values calculated using a mixture of body-centered-tetragonal [space group $I4/mmm$ with $a=3.669(3)$ Å, $c=3.295(4)$ Å] and hexagonal-close-packed [space group $P6_3/mmc$ with $a=3.150(1)$ Å, $c=5.181(2)$ Å] cells. I_{obs} for each phase is the Reitveld-decomposed value.

d_{obs} (Å)	(hkl)	I_{obs} bct	I_{cal}	d_{cal} (Å)	(hkl)	I_{obs} hcp	I_{cal}	d_{cal} (Å)
2.726					100	26	23	2.724
2.593	110	54	59	2.593	002	27	27	2.594
2.456	101	100	100	2.457				
2.414					101	100	100	2.411
1.574					110	14	18	1.573
1.461	211	36	42	1.469	103	17	21	1.460
1.397	112	13	17	1.395				
1.344					112	15	21	1.345
1.318					201	11	15	1.317
1.297	220	4	7	1.297	004	2	3	1.297

TABLE II. Observed d values and intensities at 15.4 GPa compared with the d values calculated using a hexagonal-close-packed cell [space group $P6_3/mmc$ with $a=3.135(1)$ Å, $c=5.160(2)$ Å] cell. There is a shoulder in the 101 hcp reflection which is the remnant of the 101 bct reflection.

d_{obs} (Å)	(hkl)	hcp I_{obs}	I_{cal}	d_{cal} (Å)
2.708	100	19	23	2.708
2.577	002	33	27	2.577
2.399	101	100	100	2.398
1.867	102	21	16	1.867
1.564	110	16	18	1.564
1.451	103	9	21	1.451
1.336	112	9	21	1.337
1.309	201	6	15	1.310
1.288	004	2	3	1.288

phases. Tables I and II compare the observed and calculated interplanar spacings and peak intensities of the mixture phase at 14.5 GPa and the hcp phase at 15.4 GPa, respectively. Comparison of intensities indicated that the peaks corresponding to the hcp phase increased in intensity with pressure. On unloading, the ambient ph phase was recovered. The lattice parameters and intensities for the full pressure region were obtained by carrying out multiphase Reitveld refinement with the gasket region excluded. The pressure-volume data shown in Fig. 2 were fitted to a second-order Birch-Murnaghan equation of state with the bulk modulus as 59 GPa, keeping its pressure derivative fixed at 4. The variation of the axial ratio with V/V_0 for all the three phases is shown in Fig. 3. For the ph phase the axial ratio (c/a) shows almost a constant value of 0.933. The bct phase shows an increase of c/a from 0.886 at 10.9 GPa to 0.905 at 15.4 GPa. The c/a for the hcp phase varied from 1.611 at 10.9 GPa to 1.646 at 15.4 GPa. There is no superstructure/unaccounted Bragg peak either at high pressure or after the pressure cycling during which it passes through a mixed-phase region. Thus, in spite of the fact that the stoichiometry of $In_{0.25}Sn_{0.75}$ corresponds to an AB_3-type phase, there is no evidence from the diffraction data of any ordering in the alloy under pressure. We find a volume discontinuity of about 2% at the ph to the mixed-phase transition.

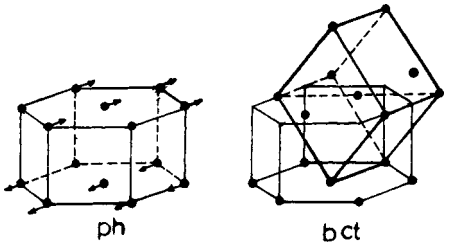

FIG. 4. Relation between primitive hexagonal (ph) and body-centered-tetragonal (bct) crystal lattices.

The existence of different intermediate structure (i.e., *Cmca* and *I*4/*mmm*) between the ph and hcp phases may also be rationalized by the fact noted by Ivanov *et al.*[25] that in the ph phase a number of low-frequency modes exist. For example, the transformation from ph to bct structure can be brought about by a softening of the T_y mode with $q=(1/200)$. Both shuffle and small homogenous distortions are required (see Fig. 4). The so-produced bct lattice would be the same, which occurs for tin above 9 GPa. The bct phase can then be transformed to the hcp phase by Buerger's mechanism.

The present study shows a reversible transition of the alloy $In_{0.25}Sn_{0.75}$ from the low-pressure ph phase to a mixture of ph, bct, and hcp phases to a mixture of bct and hcp phases. A complete transformation to the hcp phase is expected at higher pressures. This is in contrast to the behavior of light group-IV elements Si and Ge where the ph phase is seen to transform at higher pressure to close-packed structures via an orthorhombic (*Cmca*) phase. Our results are similar to the x-ray diffraction results of Degtyareva *et al.*[21] on $In_{0.20}Sn_{0.80}$. The occurrence of the bct phase in the present alloy shows a similarity to the high-pressure behavior of the heavier group-IV element Sn.

The measurements were carried out at ELETTRA under Proposal No. 1999389. Financial assistance from DST is acknowledged. We thankfully acknowledge Dr. E. Bussetto, Dr. A. Lausi, and Dr. Adolfo Savoia for their help in carrying out the experiment at ELETTRA.

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