# Evidence of polymorphic transformations of Sn under high pressure*

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The high-pressure polymorphs and structural transformation of Sn were experimentally investigated using angle-dispersive synchrotron x-ray diffraction up to 108.9 GPa. The results show that at least at 12.8 GPa $\beta$-Sn→bct structure transformation was completed and no two-phase coexistence was found. By using a long-wavelength x-ray, we resolved the diffraction peaks splitting and discovered the formation of a new distorted orthorhombic structure bco from the bct structure at 31.8 GPa. The variation of the lattice parameters and their ratios with pressure further validate the observation of the bco polymorph. The bcc structure appears at 40.9 GPa and coexists with the bco phase throughout a wide pressure range of 40.9 GPa–73.1 GPa. Above 73.1 GPa, only the bcc polymorph is observed. The systematically experimental investigation confirms the phase transition sequence of Sn as $\beta$-Sn→bct→bco→ bco + bcc→bcc upon compression to 108.9 GPa at room temperature.

**Keywords:** high-pressure, polymorph, structural transformation, Sn

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## 1. Introduction

The group IVa elements (C, Si, Ge, Sn, Pb) occupy the boundary between semiconducting and insulating behavior in the periodic table. Among them, Sn locates at the borderline between the semiconducting elements (C, Si, Ge) with the tendency to form strong $sp^3$ tetrahedral bonds and the heavy metallic element (Pb) with d orbitals participation in the bonding.[1–3] Because of the special bonding, Sn exhibits a complicated phase transition sequence under finite temperatures and pressures. Below 286 K, Sn is in a diamond-structured $\alpha$-Sn phase (or Sn–I, $Fd$-3$m$).[4] With increasing temperature, $\alpha$-Sn becomes unstable and transforms into a metallic $\beta$-phase (or Sn–II, $I4_1/amd$). Increasing the temperature further, the $\beta$-Sn melts into liquid phase at 504.9 K. Applying pressure at ambient temperature, the $\beta$-phase firstly transforms into another body-centered tetragonal structure (bct) $\gamma$-Sn (or Sn–III, $I4/mmm$) at 9.5 GPa–10.3 GPa,[5–7] and then transforms into a body-centered cubic structure (bcc, $Im$-3$m$) above 40 GPa.[6–8] Under higher compression up to 157 GPa, the bcc Sn finally transforms into a denser hexagonal close-packed (hcp, $P63/mmc$) structure.[9]

Recently, an experimental observation by Salamat *et al.*[10] indicated that bct-Sn did not transform directly into the bcc phase, but via an intermediate body-centered orthorhombic (bco, $Immm$) phase at 32 GPa. The bco structure is typically characterized by the symmetrical broadening of the full width at half maximum (FWHM) of the 200 and 211 Bragg peaks relative to the bct phase. Above 40 GPa, the bco phase partly transforms into the bcc phase and coexists with it in a wide pressure range of 40 GPa∼70 GPa. Unfortunately, the poor quality in the FWHM data of the reflections in their experiment[10] weakens the reliability of their conclusion to a certain extent. To conclude the appearance of a new phase only by symmetrical broadening of Bragg peaks is somewhat insufficient, because an unexpected bridging of the sample between diamond anvils also can lead to anisotropic broadening due to strong uniaxial stress. The non-hydrostatic stress induced by pressure-transmitting media (PTMs) also could lead to the same effect. Additionally, Salamat *et al.*[10] observed that the original $\beta$-phase and the high-pressure bct phase coexist metastably up to 15.7 GPa, whereas other previous studies[5–7] reported an onset pressure of the bct phase at 9.5 GPa with a smaller region of coexistence up to only 10.3 GPa. Nevertheless, there are no further measurements having been made to investigate the difference between the transition and finished pressures in all of these studies.[5–7,10]

Consequently, it is necessary to reinvestigate the high-pressure crystal structures of Sn to clarify its phase transition behavior under compression. Here we applied a combination of high-resolution synchrotron angle-dispersive x-ray

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diffraction (ADXRD) and diamond anvil cell (DAC) loading to systematically investigate the polymorphism of Sn up to 108.9 GPa. This work clearly observed the formation of a new orthorhombic structure from the bct structure at 31.8 GPa and confirmed the phase transition sequence of Sn as $\beta$-Sn→bct→bco→bco + bcc→bcc. The study also highlights the general aspects of the experimental approach to explore such phase transformations.

## 2. Experimental detail

High-pressure experiments were carried out using modified Mao-Bell type DAC with two beveled diamond anvils (120-μm central flat beveled at 7° angle from the 260 μm culet). The rhenium gaskets with an initial thickness of 250 μm were preindented to ∼ 20 μm and a sample chamber with a diameter of ∼ 50 μm was drilled in the center. The polycrystalline Sn sample was scalpeled from tin rod (99.98%, Alfa Aesar) and then loaded into the sample chamber along with a ruby ball as the pressure indicator.[11] Silicon oil (run 1) and argon (run 2) were used as PTMs in the two experimental runs, respectively. *In situ* high-pressure ADXRD was performed at beamline ID 4W2 at the Beijing Synchrotron Radiation Facility (BSRF). The x-ray was monochromatized to 0.6199 Å, a wavelength expected to detect the splitting of diffraction Bragg peaks, which is important for probing the bco structure. The x-ray beam was focused down to an FWHM of 13 μm×20 μm by Kirkpatrick–Baez mirrors. Data were collected using a Pilatus 2M detector. The sample-detector distance and the correction for instrumental broadening were calibrated using a $CeO_2$ standard from NIST (SRM 674a) using FIT2D.[12] All of the measurements were conducted at room temperature. ADXRD data were analyzed using FIT2D[12] and EXPGUI GSAS.[13]

## 3. Results and discussion

The Rietveld refinement of the x-ray-diffraction pattern collected at 12.8 GPa in run 1 is shown in Fig. 1. All diffraction peaks can be indexed to the bct structure except for the two from the rhenium gasket. That means the phase transformation from the $\beta$-phase to high-pressure bct phase has finished at a pressure lower than 12.8 GPa. This result is close to that of Liu *et al.*[7] who reported an onset of the bct phase at 9.7 GPa with a small coexistence region up to 10.3 GPa. But this result is quite different from that of Salamat *et al.*[10] who observed the two polymorphs coexistence up to 15.7 GPa. The relative difference of the finished pressure in $\beta$-Sn→bct transition reaches ∼ 23% between this work and Salamat *et al.*'s study. Generally, the PTMs, pressure indicators and/or sample conditions are possible causes for the discrepancy. It is well known that nonhydrostatic conditions could lower the transition pressure[14–17] compared to hydrostatic and quasihydrostatic conditions. In run 1, we used silicon oil as PTM and Salamat *et al.* using helium and neon. Upon compression, silicon oil freezes at a relatively lower pressure and gradually develops larger nonhydrostatic stress than helium and neon.[17,18] The non-hydrostatic stress often results in shear stress in the local sample region and the latter is one of the most important reasons to lower phase transformation pressure.[14] Furthermore, the systematic difference between the calibration relationships of ruby[11] (this work), tungsten,[19,20] and $SrB_4O_7$:$Sm^{2+}$[21,22] (Salamat *et al.*) are another possible reason for the large discrepancy. Finally, defects in the original sample also could contribute to the discrepancy. In run 1, an obvious texture is observed. On the one hand, texture means the sample has suffered plastic strain and permanently generated a large amount of defects during the plastic deformation, which could become the nucleation sites of new phase and significantly reduce the initial transformation pressure and accelerate the transition accomplishment.[14,23] On the other hand, texture means grains orient along the minimum stress directions and then reduce the internal stress in the material. Such reduction in stress could impede progression of transformation and a higher applied load is needed to finish the transition. Similar results can be found between $\alpha$ and $\omega$ phase transition in zirconium.[24] The observed partial reduction in the initial transformation and the finished pressure is a balance between the increased driving of the strain-induced defects to nucleate of the new phase and the increased resistance to the phase interface motion generated by change of grains orientation.

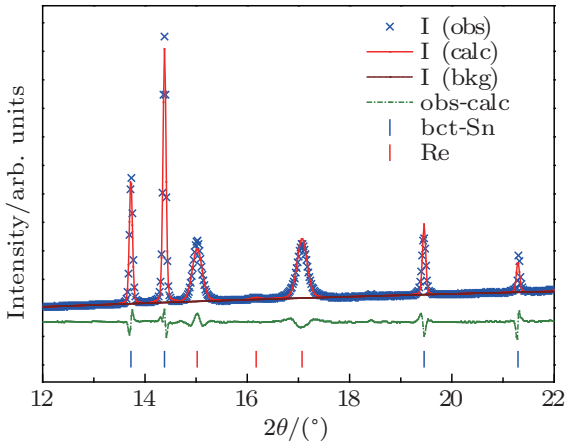



**Fig. 1.** (color online) Refinement of the x-ray diffraction pattern at 12.8 GPa by GSAS. The vertical thick lines mark the locations of the diffraction peaks from bct-Sn and the vertical thin lines show those from the rhenium gasket. The bottom curve is the difference taken from the actual spectra minus the structural refinement.

With increasing pressure, the bct structure keeps stable till a distinct change in the x-ray diffraction pattern is observed at 31.8 GPa (Fig. 2). Above 31.8 GPa, the bct 211 diffraction peak becomes asymmetrical and splits. The diffraction

patterns can be more precisely fitted to a bco structure (refinement indices $wRp$ and $Rp$ values are 2.04% and 1.39%, respectively) than bct structure ($wRp$ and $Rp$ values are 3.59% and 2.13%, respectively). The results are in good agreement with those of Salamat *et al.*[10] They found that above 32 GPa the diffraction data were fitted well by Le Bail refinement using a bco structure solution. Differently, we experimentally observed the diffraction pattern of the high-pressure orthorhombic phase in well resolved peak splittings rather than line broadenings. It is important that a long-wavelength x-ray (0.6199 Å, compared to the 0.3738 Å in Salamat *et al.*'s work) was used in the experiments, which allowed us to observe the splitting of 211 reflection. With longer x-ray wavelength, the degenerated diffraction peaks are prone to separate and thus can be distinguished in the diffraction patterns. Similarly, Ding *et al.*[25] found a second-order displacive phase transformation from cubic to rhombohedral in vanadium characterized as diffraction peaks broadening. Later Jenei *et al.*[26] made a careful investigation by using a longer-wavelength x-ray and further confirmed the phase transition. Consequently, this work also highlights an experimental approach to explore such phase transformation characterized as splitting diffraction peaks induced by lattice distortion and symmetry reduction.

The observed asymmetrical change and splitting of the 211 diffraction peak confirm the bct→bco structure transformation. The x-ray diffraction patterns might suggest the structural transition is second-order between the bct and the bco polymorphs. The symmetry was reduced from tetragonal to orthorhombic with the presence of an orthorhombic distortion and loss of the $-4$ rotation axis.

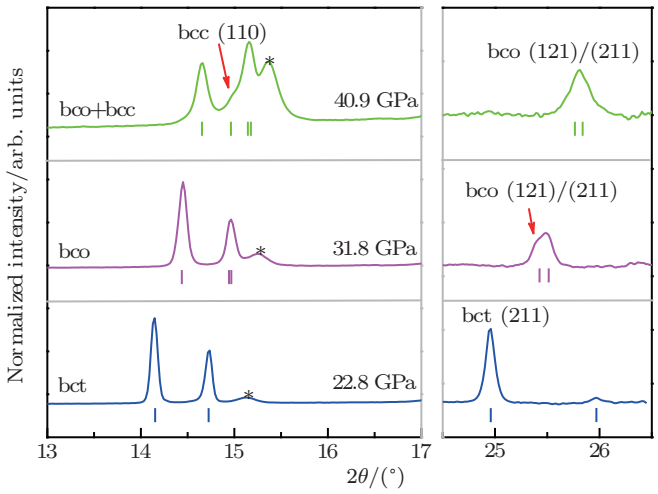



**Fig. 2.** (color online) X-ray diffraction patterns at 22.8 GPa, 31.8 GPa, and 40.9 GPa, respectively. The vertical lines indicate the location of the diffraction peaks from Sn. The asterisks indicate the diffraction peaks from the rhenium gasket. The arrow in the left panel marks the location of the 110 peak of the bcc phase. The arrow in the right panel marks the location of the splitting peaks 121 and 211 of the bco phase.

The lattice parameters and their ratios as a function of pressure are presented in Fig. 3. Between 12.8 GPa and 31.8 GPa, the $c/a$ ratio increases stably from 0.915 to 0.934 while the $b/a$ ratio remains constant 1.000. These results indicate that the lattice is under a stable tetragonal compression. With compression up to 40.9 GPa, the $c/a$ ratio continuously increases to 0.942 and keeps almost the same trend with that below 31.8 GPa. However, above 31.8 GPa a systematic difference in the compressibility between $a$ and $b$ axes occurs and the $b/a$ ratio jumps to 1.004 and then slightly increases up to 1.006 at 40.9 GPa. That suggests a new phase transformation at 31.8 GPa, which is in accordance with the observation of the x-ray diffraction patterns. The experimental data of Salamat *et al.*[10] are also plotted in Fig. 3 for comparison. It can be seen that both our $c$ and $c/a$ are in good agreement with theirs in the whole pressure range shown in Fig. 3. For bct structure, the $a$ and $b/a$ also match well. For bco structure, though $b/a$ as a function of pressure still keep coincident, $a$ and $b$ in this work are somewhat larger than those measured by Salamat *et al.* Again, the different PTMs and pressure indicators are possible reasons for the discrepancy. It should be noted that $b$ at 39.7 GPa and 40.8 GPa measured by Salamat *et al.*[10] are relatively small and result in abnormal $b/a$ values, which may be caused by the poor measurement accuracy in the vicinity of the transformation pressure.

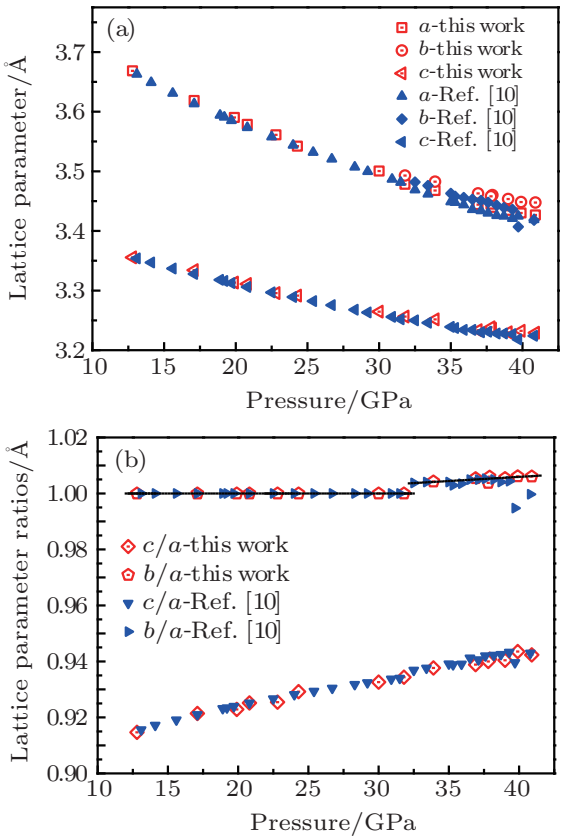



**Fig. 3.** (color online) The lattice parameters $a$, $b$, $c$ (a), and their ratios $c/a$ and $b/a$ (b) as a function of pressure. The open symbols denote the data in this work and the solid ones denote those from Ref. [10]. The dashed lines are guides to the eye.

Above 40.9 GPa, the x-ray diffraction data show the appearance of an additional peak (Fig. 2) at about 15° in diffraction angle. The new diffraction peak can be fitted well using a bcc structure solution. The result indicates the presence of the transformation from the bco structure into a bcc structure at 40.9 GPa, which is in good agreement with 40 GPa∼44 GPa reported in previous studies.[6,7,10] With further compression, the diffraction peaks of the two phases remain concomitant until 73.1 GPa at which the diffraction peaks related to bco structure completely vanish. Salamat *et al.*[10] reported coexistence of the bco and bcc structures in the 40 GPa–70 GPa range. The relative difference between the finished pressures in bco→bcc transition is about ∼ 4%, which is reasonably in accordance with our result considering the difference of the pressure indicators and PTMs. Above 73.1 GPa, the bcc structure remains stable till the highest experimental pressure 108.9 GPa in this work.

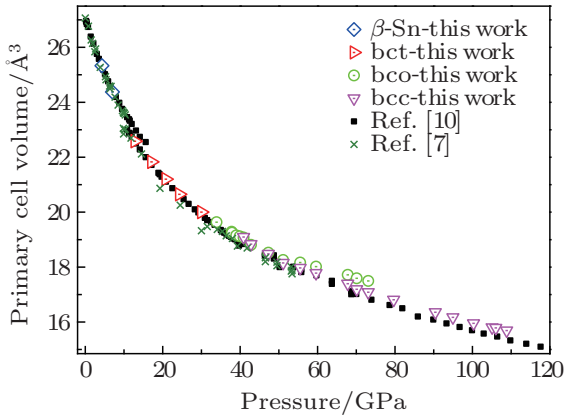



**Fig. 4.** (color online) The primary cell volume versus pressure data of Sn at room temperature. The open symbols denote the high-pressure experimental data measured in this work. The solid squares and crosses denote Salamat *et al.*'s[10] and Liu *et al.*'s[7] experimental data, respectively.

The compressive behavior of Sn up to 108.9 GPa is presented in Fig. 4. For comparison, the experimental results of Salamat *et al.*[10] and Liu *et al.*[7] are also shown in Fig. 4. When $\beta$-Sn transformed into bct structure, the volume collapse is approximately 2%, which is consistent with that of Salamat *et al.*[10] and Liu *et al.*[7] However, the bct→bco phase transition does not demonstrate a distinct discontinuity in the volume-pressure data and thus bct→bco might be a second-order phase transition. Although Liu *et al.* did not find the bct→bco structure transformation in their study, the given compressibility of Sn in 32 GPa∼40 GPa still agrees well with that of Salamat *et al.* and this work. That indicates an ignorable difference in compressibility between bct phase and bco phase. For bco→bcc phase transition, the volume reduction is also not so obvious, but with increasing pressure the bcc phase represents a larger compressibility than the bco phase. Above 73.1 GPa, the compressibility of bcc Sn has a systematic deviation between this work and that of Salamat *et al.* That could be accounted for by the nonhydrostaticity of PTMs.[17] In summary, Sn has experienced the phase transition sequence of $\beta$-Sn→bct→bco→bco + bcc→bcc under compression up to 108.9 GPa.

## 4. Conclusions

This study presents a systematic experimental investigation of the high-pressure polymorphism of polycrystalline Sn in a DAC. The results reveal an unusual high-pressure structural transformation of Sn in the 4.3 GPa–108.9 GPa range. At least at 12.8 GPa, $\beta$-Sn has accomplished the transition into high-pressure bct structure, and the suggested coexistence of the two phases is not observed. The large discrepancy of the finished pressure of $\beta$-Sn → bct phase transformation in the studies is attributed to a combined effect of the texture of the original sample, the PTMs and pressure indicators. By using a longer-wavelength x-ray, a directly experimental observation clearly demonstrate the splitting of the 211 diffraction peak and validate the formation of a new orthorhombic structure from the bct structure at 31.8 GPa. The characters of the splitting x-ray-diffraction peaks and the continuity in the volume-pressure data both suggest that the phase transition between the bct and bco polymorphs might be second-order. That also suggests an experimental approach to explore such phase transition characterized as asymmetrical and splitting diffraction peaks induced by lattice distortion. The experimental observation demonstrates the bco and bcc structures coexist throughout a wide pressure range of 40.9 GPa–73.1 GPa and confirms the phase sequence as $\beta$-Sn→bct→bco→bco + bcc→bcc of Sn under compression up to 108.9 GPa.

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