

INCOMMENSURATE MODULATIONS IN THE STRUCTURE OF Bi-III

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The crystal structure of Bi-III, stable between 2.8 and 7 GPa, has long been known to be complex and has attracted much attention. Although previously described as orthorhombic or tetragonal, we have recently shown [1] that Bi-III is in fact incommensurate, comprising a body-centred tetragonal (bct) 'host' and a bct 'guest' component made up of chains that lie in channels in the host; the guest is incommensurate with the host along the tetragonal c-axis.

In our powder-diffraction patterns of Bi-III, we identified two additional very weak peaks that we speculated may arise from a further modulation of the host or guest structures [1]. To confirm the origin of these satellite peaks, we have performed a single-crystal study of Bi-III at 4.5 GPa in which more than 200 of these satellite reflections were located and their intensity measured. Using the satellite reflections, it has been possible to perform a full 4-dimensional refinement of the Bi-III crystal structure, and thereby model the modulations of the host and guest structures. The full Bi-III structure will be presented.

References

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Keywords: HIGH PRESSURE CRYSTAL STRUCTURES INCOMMENSURATE

PRESSURE-INDUCED AMORPHOUS-AMORPHOUS TRANSITION IN MOLECULAR SOLID SnI₄

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A metallic amorphous form of SnI₄ is induced by compression above 15 GPa at room temperature. Our recent study showed that the SnI₄ molecules no longer existed above 35 GPa in the amorphous state and that measured diffraction profiles exhibited many features of the amorphous structure formed by the dense random packing of hard spheres (DRPHS). Above 61 GPa, amorphous SnI₄ transforms to a non-molecular crystalline phase. When the crystalline phase is decompressed, the amorphous state reappears at 30 GPa. We found that on further decompression the first diffraction peak shifted discontinuously between 2.3 GPa and 4.1 GPa. On the subsequent compression, the jump in the reverse direction took place at 5.8 GPa. These observations suggest the occurrence of structural changes in the amorphous state. We here report a synchrotron x-ray diffraction study of changes in atomic-scale structure of amorphous SnI₄.

Diffraction patterns were measured at 2.5 GPa on the first decompression from 29 GPa and at 8.1 GPa and 15 GPa on the second compression. We obtained the Faber-Ziman structure factor S(Q) at each pressure and the reduced radial distribution function G(r) by sine transform of S(Q). In G(r) at 2.5 GPa, peaks corresponding to the intramolecular atomic distance, Sn-I and I-I, were clearly observed. At 8.1 GPa and 15 GPa, the Sn-I distance was found to increase and the peak at the I-I distance disappeared, indicating breakup of the SnI₄ molecules. These observations lead us to conclude that the pressure-induced structural change in amorphous SnI₄ is a phase transition characterized by the molecular dissociation.

Keywords: MOLECULAR CRYSTAL PRESSURE-INDUCED AMORPHIZATION SYNCHROTRON X-RAY DIFFRACTION

COMPLEX METAL STRUCTURES AT HIGH PRESSURES

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We have recently found many new complex structures in Rb, Cs, Sr, Ba, Ga, As, Sb, Bi and other metallic elements. In some cases, these structures comprise two interpenetrating components - one a 'host' framework and the other a 'guest' structure made up of chains that occupy channels in the host - that are incommensurate with each other. In the group V elements, these components are not only incommensurate with each other but also are modulated, giving rise to additional satellite reflections. In other cases, the complexity is expressed as a superstructure of a simpler structure. And in yet other cases, there is a complex stacking of different layers - which may be understood as another form of modulation. In this presentation, we will present an overview and explore key aspects of the emerging systematics of these remarkable new structures, some of which have of the order of 100 atoms in the unit cell.

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CRYSTAL STRUCTURE OF A HIGH-PRESSURE PHASE OF ZrP₂O₇

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Over the past several years there has been substantial interest in the properties of phases with compositions such as ZrV_{2-x}P_xO₇ or TiV₂O₇, especially because of their negative thermal expansion (1). Thus, most investigations have been conducted at room pressure with increasing temperature although Carlson and Andersen (2) reported a phase transition in ZrV₂O₇ at 1.38-1.58 GPa, but no transition in ZrP₂O₇ to 40.3 GPa at ambient temperature. However, Sclar et al. (3) had previously reported the synthesis of a high-pressure phase of ZrP₂O₇ at pressures up to 10 GPa and 750-1000°C, so we synthesized a polycrystalline sample of this phase with the composition ZrP₂O₇ (ZrP₂O₇ II) at 7 GPa and 800°C in a multi-anvil apparatus. Powder x-ray data were recorded at beamline X7A of the National Synchrotron Light Source. Its unit-cell parameters are a = 7.538 Å, c = 7.301 Å, V = 359.3 Å³, and Z = 3. We solved the structure assuming space group P31 and found that it consists of ZrO₆ octahedra and PO₄ tetrahedra linked in a similar way to the 1 atmosphere structure of ZrP₂O₇ I, but with a 17% higher density. Examination of the structure plus structure refinement indicated additional symmetry elements consistent with space group P3121.

References

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