Supporting Information of

The Pressure-Stabilized Polymorph of Indium Triiodide

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Experiments

The ambient-pressure phase of monoclinic InI_3 was purchased (from Alfa Aesar, anhydrous, 99.999%) and used as the starting material for the high-pressure synthesis. To do that synthesis, the ground powder of the starting material was loaded into a boron nitride crucible in an air-free atmosphere, inserted into a pyrophyllite cube assembly and pressed to 6 GPa using a cubic multi-anvil system (Rockland Research Corporation). The sample was annealed at 500 °C for 3 hours. The pressure applied through the multi-anvil system was determined by the standard curve method and calibrated with a standard substance before conducting experimental synthesis, and the temperature was measured by an internal thermocouple. The system was quench-cooled to room temperature before decompression. The products obtained were reddish in color, from which small single crystals were taken for SCXRD characterization. The ground powder of the post-reaction sample shows an orange-red color, which is different from the light-yellow color of the monoclinic InI_3 starting material.

Due to the air-sensitivity and hygroscopicity of the materials, the PXRD patterns used for structural characterization were collected using a Rigaku Miniflex II diffractometer located inside a nitrogen-filled glove box for both the starting material and the products, with Cu Kα radiation (λ= 1.5406 Å) employed. Le Bail fitting was performed on the starting material pattern to confirm its uniformity (via TOPAS software), while a full Rietveld refinement was performed via GSAS II on the high-pressure-synthesis product diffraction pattern for structural analysis.

To determine the space group symmetry and cell parameters, a crystal of HP-InI_3 with dimensions 0.216 × 0.105 × 0.084 mm^3 was picked up, mounted on a nylon loop with paratone oil, and characterized using a XtalLAB Synergy, Dualflex, Hypix single crystal X-ray diffractometer with an Oxford Cryosystems low-temperature device, operating at T = 300(2) K. The diffraction data were collected using ω scans with Mo Kα radiation (λ= 0.71073 Å, micro-focus sealed X-ray tube, 50 kV, 1 mA). The total number of runs and images was based on the intensity collection strategy calculation from the program CrysAlisPro 1.171.42.79a (Rigaku OD, 2022). Cell parameters were retrieved and refined based on 5708 reflections, 50.6% of those

observed. Data reduction was performed with correction for Lorentz polarization. A numerical absorption correction based on gaussian integration, as implemented in SCALE3 ABSPACK was applied. The SHELXTL Software Package[1,2], was used to determine the space group as $R\bar{3}$ (#148), with Z = 6, and an approximate crystal structure. The SCXRD data, which help to determine the symmetry and the initial unit cell parameters, were then used as a starting point for Rietveld refinement of the PXRD pattern.

Magnetization and heat capacity were measured using a Quantum Design PPMS (Dynacool), equipped with a vibrating sample magnetometer (VSM) option. The temperature-dependent magnetization (M) was measured in an applied magnetic field (H) of 1000 Oe. UV-Vis diffuse reflectance spectra are collected using an Agilent Cary 5000 spectrometer with Agilent Internal DRA-2500 diffuse reflectance accessory on powder samples. Samples were diluted with dry MgO to 50% w/w, while dry MgO is used as the reflectance standard. The band gap values are calculated using Tauc plots, while reflectance data were converted to absorption using the Kubelka-Munk function. Transfers of samples to the measurement apparatus were performed very rapidly to protect the sample from hydrolysis. Both AP- and HP-InI_3 are air-sensitive and hygroscopic. They absorb moisture in the air and change into a white color in several minutes.

Table S1. Selected bond lengths (Å) and bond angles (°) for HP-InI_3 at 300 K, obtained from Rietveld refinement. Standard deviation is indicated by the values in parentheses.

Bond Length (Å)	In2-I1 (x2)	2.910(9)
	In2-I1 (x2)	2.904(9)
	In2-I1 (x1)	2.911(9)
	In2-I1 (x1)	2.905(9)
Bond Angle (°)	I1-In2-I1 (x3)	87.5(4)
	I1-In2-I1 (x3)	88.48(7)
	I1-In2-I1 (x3)	90.0(4)
	I1-In2-I1 (x3)	86.54(2)
	I1-In2-I1 (x1)	175.62(22)
	I1-In2-I1 (x1)	175.63(21)
	I1-In2-I1 (x1)	175.65(22)

References

1 G. M. Sheldrick, *Acta Crystallographica Section C Structural Chemistry*, 2015, **71**, 3–8.
2 G. M. Sheldrick, *Acta Cryst A*, 2015, **71**, 3–8.