Pressure-induced decomposition of indium hydroxide

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High pressure behavior of indium oxide (In$_2$O$_3$) has recently gained particular attention [1-3]. Despite progress achieved in recent years both in theoretical prediction of phase transitions in In$_2$O$_3$ and experimental realization of new In$_2$O$_3$ polymorphs, the complete pressure-temperature diagram of indium oxide is still lacking. Even less is known about high pressure behavior of indium hydroxide. Indium hydroxide, c-In(OH)$_3$, has so-called A site deficient hydroxyl-perovskite structure (space group $Im$
$3$, No. 204, a = 7.979 Å, Z = 8). c-In(OH)$_3$ has been considered as a promising precursor for synthesizing new high pressure In$_2$O$_3$ polymorphs. The main goal of the present work was to study the high-pressure behavior of indium hydroxide at pressures exceeding 1 GPa. We have performed in situ high-pressure X-ray diffraction experiments on c-In(OH)$_3$ with controlled crystal morphology and size [4]. Samples were compressed in diamond anvil cells (DAC) up to ~ 32 GPa at room temperature. In situ X-ray diffraction experiments were performed in diamond-anvil-cells (DAC) up to ~ 32 GPa in the energy-dispersive mode at the F3 beamline of the HASYLAB (DESY, Hamburg, Germany). No phase transitions have been observed in In(OH)$_3$ during compression; decompression, however, leads to the decomposition of c-In(OH)$_3$ into metallic indium, water and oxygen. The instability of the c-In(OH)$_3$ as well as of any other metal hydroxide /oxohydroxide towards decomposition under high pressure conditions has never been reported before.

As we reported recently [4], on heating up to 300°C in air under ambient pressure conditions c-In(OH)$_3$ (a = 7.98 Å) transforms irreversibly to c-In$_2$O$_3$. This phase transition is accompanied by the fragmentation of c-In(OH)$_3$ cube-shaped crystals and can be easily followed even visually since c-In(OH)$_3$ is white and c-In$_2$O$_3$ is yellow in color. During compression up to ~ 32 GPa at room temperature neither phase transitions nor colour change have been observed in c-In(OH)$_3$ (Figure 1, C-D); the compression only leads to continuous shift and broadening of c-In(OH)$_3$ reflections (Figure 2).

![Figure 1](image)

Figure 1. Optical microscope images of c-In(OH)$_3$ samples loaded in Re-gasket with Pt-pieces in DAC: initial at ambient pressure (A, B), that at 32 GPa (C, D), and recovered to ambient conditions (E, F).

The broadening of the reflections is most probably caused by c-In(OH)$_3$ amorphization during compression. The shift of reflections to higher energy indicates a decrease in the lattice parameter of c-In(OH)$_3$ which is about 7.40 Å at 32 GPa. During prompt decompression the c-In(OH)$_3$
samples have been changing their colour, becoming either blackened or reddened (Figure 1 E and D) depending on the decompression conditions. Simultaneously, two broad reflections at ~ 32 keV (d ~ 2.533 Å) and at ~ 51.9 keV (d ~ 1.562 Å) appeared in a diffraction pattern of recovered c-In(OH)₃ samples; those reflection were not observed in initial as well as compressed samples. The aforementioned reflections can be attributed to those of metallic tetragonal indium (space group \textit{I}₄/\textit{mmm}, No. 139, a=5.26 Å, b=4.56 Å, a=3.27 Å, c=1.5211 Å, Z = 2). The presence of In-reflections in XRD pattern indicates the partial decomposition of indium hydroxide to metallic indium, oxygen and water.

![Figure 2](attachment:image.png)

**Figure 2.** In situ ED-XRD patterns of c-In(OH)₃ in DAC at ambient pressure (initial and recovered) and at high pressures up to 32 GPa.

The mechanism of c-In(OH)₃ decomposition could be explained as follows. During compression to ~ 32 GPa c-In(OH)₃ was overpressed in the region where its structure is metastable. Kinetic factors prevent its transition into either o-InOOH or In₂O₃. The compression resulted in dissimilar shift of indium and oxygen atoms in c-In(OH)₃ lattice; this dissimilarity is expressed in stronger broadening of the reflections of the planes composed of In-atoms. This suggestion is confirmed by a large broadening of \{220\} reflections in the c-In(OH)₃ structure. In the space group \textit{Im}₃ the \{220\} reflections are attributed to the planes of atoms in the 8c positions (¼, ¼, ¼). In the c-In(OH)₃ structure these position are occupied by In-atoms. During decompression, the relaxation of indium atoms towards equilibrium positions resulted in the more favourable In-structural positions in tetragonal indium.

Summarizing, no phase transitions have been observed in c-In(OH)₃ during compression up to ~ 32 GPa at room temperature. The decompression leads to the decomposition of c-In(OH)₃ into metallic indium, water and oxygen. The instability of the c-In(OH)₃ as well as of any other metal hydroxide /oxohydroxide towards decomposition under high pressure conditions has never been reported before.

**Acknowledgements**

The financial support by DESY (proposal 1-20080181) and the DFG Priority Programme 1236 „Oxides, carbides and nitrides at extremely high pressures and temperatures“ (SPP 1236) is gratefully acknowledged.

**References**