Kinetic Control in the Synthesis of Metastable Polymorphs: Bixbyite-to-Rh$_2$O$_3$(II)-to-Corundum Transition in In$_2$O$_3$

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Indium oxide (In$_2$O$_3$) - a transparent semiconductor with intrinsic n-type character - serves as a base material for diverse applications including touch displays and photovoltaics, thermoelectrics, and gas sensors. The structure-property study in different In$_2$O$_3$ polymorphs is of vital interest both for technology and fundamental science allowing for guiding synthetic approaches towards improved optical and electronic properties of transparent conductive oxides and development of improved electronic devices. Four In$_2$O$_3$ polymorphs have been synthesized so far, i.e. (i) cubic bixbyite-type c-In$_2$O$_3$ (C-type structure of rare-earth oxides, Ia-3, No. 206), (ii) rhombohedral corundum-type rh-In$_2$O$_3$ (space group R-3c, No. 167), (iii) orthorhombic Rh$_2$O$_3$-II-type o$^1$-In$_2$O$_3$ (Pbcn, No. 60), and (iv) orthorhombic α-Gd$_2$S$_3$-type o$^\alpha$-In$_2$O$_3$ (Pnma, No. 62). c-In$_2$O$_3$ and rh-In$_2$O$_3$ are accessible through solution-based and solvothermal routes;$^1$ α-Gd$_2$S$_3$-type o$^\alpha$-In$_2$O$_3$ is attainable at pressures over 19.9 GPa and transforms to rh-In$_2$O$_3$ upon decompression.$^2,3$ Synthesis and stability of rh-In$_2$O$_3$ and o$^\alpha$-In$_2$O$_3$ face some controversy. In all reported works the conclusions about the phase transitions of these two polymorphs as well as about the stability of rh-In$_2$O$_3$ under HP-HT conditions were drawn from the identification of the quenched products. Prewitt et al.$^4$ assumed that “the presence of large crystals suggests that rapid reconstructive transformation did not take place”. Recent in-situ studies in the LH-DAC report the rh-In$_2$O$_3$ as a minor side phase which coexists with o$^\alpha$-In$_2$O$_3$ at 5.2-8.1 GPa and 1700 K (1400 °C).$^5$ According to ref. [5] o$^1$-In$_2$O$_3$ is stable in the pressure range between 8.1 and 19.9 GPa, but ultimately transforms to rh-In$_2$O$_3$ upon decompression. In contrast, we succeeded to recover it from ~ 30 GPa to ambient pressure and temperature in a laser-heated diamond anvil cell experiment.$^3$ However, due to a very limited amount of the specimen (a few crystals, < 10$^{-4}$ mm$^3$) the crystal structure of o$^\alpha$-In$_2$O$_3$ at ambient conditions was not unambiguously confirmed.

In our work we aim to construct the apparent pressure-temperature phase diagrams and discuss the stability fields of the three low pressure polymorphs c-In$_2$O$_3$, rh-In$_2$O$_3$ and o$^\alpha$-In$_2$O$_3$ and the crystallographic relationship between them. We followed the formation of metastable rhombohedral and orthorhombic In$_2$O$_3$ polymorphs in situ under high-pressure high-temperature conditions via energy-dispersive X-ray diffractometry at the two stage 6-8 MAX200X multianvil high pressure diffractometer of the GFZ Potsdam (beamline W2). New high-pressure/high-temperature multi-anvil assemblies for synchrotron studies developed at the Freiberg High Pressure Research Centre were employed.$^6$ These assemblies have low X-ray absorption and don’t show any additional reflections from the sample environment.

Figure 1a displays the in-situ energy-dispersive X-ray diffraction patterns of a c-In$_2$O$_3$ specimen compressed to 8.5 GPa and heated up to 850 °C. XRD patterns observed between
ambient pressure and 8.5 GPa at room temperature correspond to c-In$_2$O$_3$. At 850 °C, the peak intensity of c-In$_2$O$_3$ is significantly reduced and a series of new reflections characteristic for the orthorhombic $\alpha'$-In$_2$O$_3$ polymorph appears. The complete phase transition c-In$_2$O$_3 \rightarrow \alpha'$-In$_2$O$_3$ takes less than 30 seconds at 8.5 GPa / 850 °C. The XRD pattern of the specimen rapidly quenched from 850 °C to room temperature shows only $\alpha'$-In$_2$O$_3$ reflections. During decompression at room temperature, $\alpha'$-In$_2$O$_3$ transforms to rh-In$_2$O$_3$ at 5.5 GPa. The structure refinement of the specimen recovered to the ambient pressure/temperature confirms the rh-In$_2$O$_3$ structure (not shown here).

Figure 1b displays the in-situ energy-dispersive X-ray diffraction patterns of a rh-In$_2$O$_3$ specimen compressed to 9.0 GPa and heated up to 600 °C. XRD patterns observed between ambient pressure and 9.0 GPa at room temperature correspond to those of rh-In$_2$O$_3$. At 600 °C, the peak intensity of rh-In$_2$O$_3$ is significantly reduced and a series of new reflections characteristic for $\alpha'$-In$_2$O$_3$ starts to appear. The complete transformation from rh-In$_2$O$_3$ to $\alpha'$-In$_2$O$_3$ take less than 20 seconds at 600 °C and 9 GPa, indicating fast kinetics for a diffusionless transition.

In contrast to the experiments with c-In$_2$O$_3$, in this experiment remnants of $\alpha'$-In$_2$O$_3$ remain after temperature quenching and decompression ambient pressure. It is interesting to note that the XRD pattern of material rapidly quenched from 600 °C to room temperature at 9 GPa possesses only $\alpha'$-In$_2$O$_3$ reflections. During decompression at room temperature, $\alpha'$-In$_2$O$_3$ partially transforms to corundum rh-In$_2$O$_3$ at pressure below 1.0 GPa. The structure refinement of the specimen recovered to ambient pressure confirms the coexistence of $\alpha'$-In$_2$O$_3$ (fraction: 80.0 wt.%), rh-In$_2$O$_3$ (15.9 wt.%) and o-InOOH (4.1 wt.%) as a side phase.

Figure 1. In-situ energy-dispersive XRD patterns of (a) c-In$_2$O$_3$ specimen compressed at 8.5 GPa and heated up to 850 °C and (b) rh-In$_2$O$_3$ specimen compressed at 9.0 GPa and heated up to 600 °C. The tick marks refer to the calculated Bragg positions of c-In$_2$O$_3$, $\alpha'$-In$_2$O$_3$ and rh-In$_2$O$_3$.