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# Structural Stability of High-Pressure Polymorphs in $In_2O_3$ Nanocrystals: Evidence of Stress-Induced Transition?[**]

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colloids · high-pressure chemistry · indium oxide · nanomaterials · phase transitions

Nanoscale phase transitions have gained particular attention especially because of the size-dependence of material properties and their influence on the functionality of nanoscale devices.[1] Several material properties such as superplasticity and ferromagnetism change as a function of crystal size; in certain cases these properties are even completely suppressed once the crystal size is smaller than a critical value. In some cases, the decrease in crystal sizes also leads to crystal structures and morphologies different from those of the bulk crystals.[2] Well-known examples include the stabilization of cubic $BaTiO_3$,[2b] anatase ($TiO_2$),[2c] tetragonal $ZrO_2$,[2g] and γ-$Al_2O_3$[2d] as nanomaterials. The change in the crystal structure also alters the material properties; thus bulk tetragonal $BaTiO_3$ is piezoelectric, but cubic nanocrystalline $BaTiO_3$ is not.

As predicted by theory[2c,e] and confirmed by microcalorimetry,[2a,f] the structural phase transitions may be arrested below a critical size because the surface energy overwhelms the bulk energy. Accordingly, in nanosystems, the stability of "bulk" polymorphs could be reversed and a low-energy polymorph—which is metastable in bulk form—becomes stable as the particle size decreases. The effects of surface stresses are also significant at the nanoscale. As the size of particles decreases, the surface stress produces an effective pressure equivalent to an external compressive pressure applied to a material. In nanoparticles, which are small enough to generate surface stress above the pressure needed for a phase transition, a high-pressure polymorph could be stabilized (Figure 1). However, the systematic interpretation whether high-pressure polymorphs could be stabilized in oxide nanoparticles under ambient pressure conditions has been limited by the lack of experimental probes. Neither $Al_2O_3$, nor $TiO_2$, nor $ZrO_2$, nor $BaTiO_3$ crystallize in high-pressure structures in nanoparticles.[3]

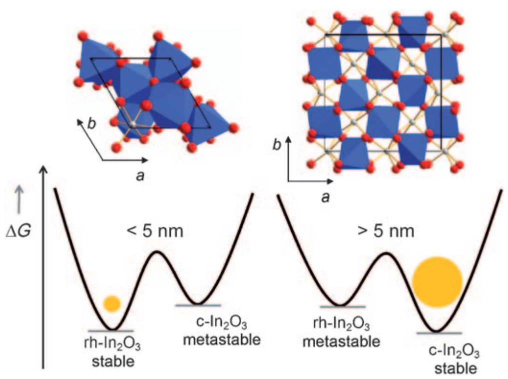

***Figure 1.*** Structures of the polymorphs rh-$In_2O_3$ (left) and c-$In_2O_3$ (right; In: small gray balls, O: large red balls) along with a representation of the potential energy diagrams for small and large particles. The high-pressure polymorph rh-$In_2O_3$ polymorph, which is only metastable in bulk form, becomes stable at smaller particle sizes decreases (see Figure 3).

Recent work by Farvid et al. on the phase-controlled synthesis of colloidal indium oxide ($In_2O_3$) nanocrystals may be an instructive example of such stress-induced stabilization of metastable high-pressure polymorphs in oxide nanoparticles synthesized in ambient pressure conditions (Figure 2).[4]

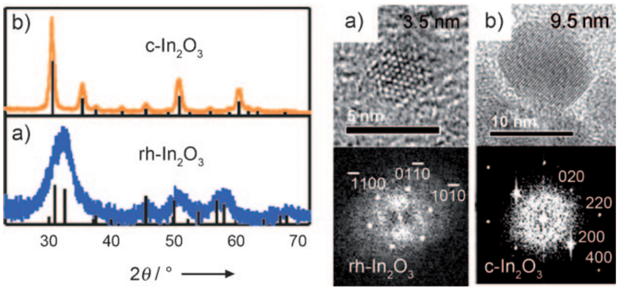

***Figure 2.*** Left: XRD patterns, right: high-resolution TEM (top) and the corresponding FFT (fast Fourier transform) images (bottom) of 3.5 nm rh-$In_2O_3$ (a) and 9.5 nm c-$In_2O_3$ crystals (b). (Copyright American Chemical Society, reproduced with permission from Ref. [4a]).

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$In_2O_3$ is a transparent n-type semiconductor with diverse applications:[5] 1) Sn-doped $In_2O_3$, known as ITO (indium tin oxide), is the key material for solar energy utilization;[5a] 2 $Cr^{3+}$-, $Mn^{3+}$-, $Fe^{3+}$-doped $In_2O_3$ are room-temperature ferromagnetics;[5b] 3 $In_2O_3$-based gas sensors show high sensitivities to toxic and explosive gases at low temperatures, such that they can be used as gas detectors on flexible electronic platforms.[5c,d]

Because of the relevance of the size-dependent phenomena to the engineering of materials with enhanced functional properties, the synthesis of well-defined nanocrystals of pure and doped $In_2O_3$ has been of considerable interest for fundamental studies as well as for technological applications. The introduction of a high-temperature synthesis using high-boiling solvents at solution temperatures over 250 °C was an important step towards the fabrication of monodisperse $In_2O_3$ nanocrystals. As demonstrated in classical studies by LaMer and Dinegar, the synthesis of monodisperse colloids by means of homogeneous nucleation requires a temporal separation of nucleation and growth stages.[6] Experimentally, the separation of nucleation and growth can be achieved by rapid injection of the reagents into the hot solvent, which raises the concentration of the precursor in the reaction flask above the nucleation threshold (hot-injection method; for details, see, for example, Ref. [7]). Another approach relies on attaining the degree of supersaturation necessary for homogeneous nucleation by the in situ formation of the reactive species upon supply of thermal energy (heating-up method).

Both methods have been utilized for the synthesis of ITO,[8] $In_2O_3$,[4,9] and TMI-$In_2O_3$,[4b] and for the formation of $In_2O_3$ supercrystals[9a] using hot solutions of indium carboxylates or indium acetylacetonate[10] with free carboxylic acid and primary amines. A combination of nucleophilic attack of the electron-deficient carbon in carbonyl groups and condensation–hydrolysis cascade reactions produced highly crystalline and monodisperse oxide nanoparticles. However, their crystal structure appeared to depend on the reaction time and dopants used. By monitoring the formation of colloidal $In_2O_3$ crystals over time, Farvid et al. succeeded in clarifying this discrepancy (Figure 1). Their surprising findings are:[4]

- The crystallization of the metastable high-pressure rh-$In_2O_3$ polymorph occurs in < 5 nm $In_2O_3$ particles at initial stages in the colloidal synthesis of c-$In_2O_3$.
- An increase in nanocrystal size to about 5 nm induces a change in the $In_2O_3$ structure from rhombohedral to cubic.
- Dopant ions like $Mn^{3+}$ (Mn:In = 0.05) inhibit the crystal growth leading to the stabilization of metastable rh-$In_2O_3$.

What causes the crystallization of high-pressure rh-$In_2O_3$ in < 5 nm nanoparticles? In the two $In_2O_3$ polymorphs indium–oxygen polyhedra are of the same type, octahedral, and have similar sizes; in all structures oxygen has nearly tetrahedral coordination.[11] This structural similarity is reflected not only in small density differences, but also in the small energetic difference: rh-$In_2O_3$ is about 2.5 % denser than c-$In_2O_3$ and the difference in enthalpy is about 15 kJ $mol^{-1}$ at ambient pressure (Figure 3).[12] Eventually at about 3.8–13.5 GPa (depending on the DFT method applied for calculation[12,13]) the enthalpy of the two phases becomes equal, indicating a phase transition from c-$In_2O_3$ to the more dense rh-$In_2O_3$. The reduction in the volume of a particle is equivalent to the excess pressure applied; the latter induces lattice contraction which is reflected in slightly higher values of $2\theta$ in the XRD patterns observed by Farvid et al.[4] The lattice contraction, which increases as the size of the nanocrystals decreases, favors the higher-density rh-$In_2O_3$ which has shorter interatomic distances. Accordingly, rh-$In_2O_3$, which is metastable in bulk form, becomes energetically favorable during the crystallization of < 5 nm particles.

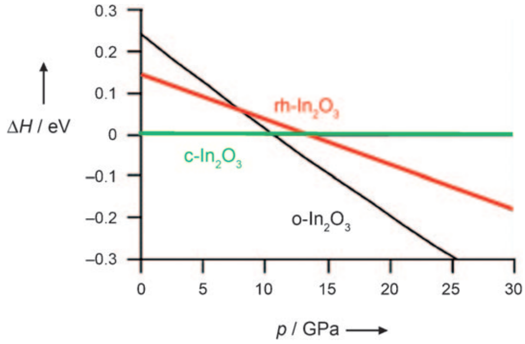

**Figure 3.** Enthalpy–pressure diagram for indium oxide polymorphs, synthesized so far, with cubic c-$In_2O_3$ (bixbyite) as a reference structure.[12] c-$In_2O_3$ (C-type structure of rare-earth oxides, space group $Ia\bar{3}$, No. 206, $Z = 16$) is thermodynamically stable under ambient pressure. Corundum-type rh-$In_2O_3$ (space group $R\bar{3}c$, No. 167, $a = 5.491$ Å, $c = 14.526$ Å, $Z = 6$) is a metastable high-pressure polymorph. Orthorhombic o-$In_2O_3$ ($Rh_2O_3$ II structure type, space group *Pbna*, No. 60, $Z = 4$) was synthesized under high-pressure high-temperature conditions in laser-heated diamond-anvil cells.[11,14]

These recent results on the colloidal synthesis of $In_2O_3$-based nanocrystals are of exceptional methodological, fundamental, and technological importance. Understanding the growth mechanism and structural transformation should allow the rational and controlled preparation of colloidal $In_2O_3$ particles having specific sizes and structures by simply adjusting the reaction conditions, including temperature, precursors, solvents, coordinating ligands, and reaction time. The synthesis methodology developed so far makes it possible to form highly crystalline, deagglomerated, and monodisperse oxide particles. Such particles—owing to their easy processability into films with high variability in terms of substrate structure and geometry—are of great interest for many applications, for example for inkjet printing of flexible electronic components. The synthesis of colloidal indium oxides utilizing heating-up and hot-injection methods in high-boiling solvents is still in its infancy when compared to the well-established synthesis of II–VI quantum dots (CdSe, CdS, CdTe etc.).[7] Nevertheless, for both classes of materials, an ongoing trend toward simplifying the synthesis procedure can be observed in view of an enhanced reproducibility and scale-up of the reactions. The large-scale one-pot (subkilogram quantities) synthesis of II–VI quantum dots has already been demonstrated;[15] that of $In_2O_3$-based nanocrystals is on the horizon. And finally, the $In_2O_3$ case study appears to be an instructive example for learning more about energetic pathways of phase transitions on the nanoscale.

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