Joint computational and experimental examination of the phase stability of $(In_xGa_{1-x})_2O_3$ ternary alloys

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In this collaboration, we investigate the key parameters determining the stability of mixtures of Ga_2O_3 and In_2O_3 alloys. Alloying allows for the tuning of a desired property over large ranges, which enables the design of new materials with ideal properties. To achieve the synthesis of high-quality alloys, an understanding of the phase formation as function of composition is required. In this project, we examine using a combination of experiment and computation of the phase diagram of the heterostructural alloy $(In_xGa_{1-x})_2O_3$, where the two components display different thermodynamic ground state crystal structures.

The growth and structural characterization of the experimentally investigated thin film materials is carried out by IKZ, PDI and Uni Leipzig. The theoretical models for the stability is developed in collaboration between HU & FHI.

Our results show that the alloy stability is determined by a competition between both the thermodynamically stable lattices of In_2O_3 (cubic phase) and Ga_2O_3 (monoclinic phase) and a high-temperature and high-pressure binary alloy (hexagonal phase). The range of stabilities at elevated temperatures of the monoclinic, hexagonal, and cubic phases are calculated to occur for the indium concentrations (x) of $x \leq 0.40$, $0.50 \leq x \leq 0.70$, and $x \geq 0.90$, respectively. For the β and h phases, indium is incorporated into a sub-lattice of six-fold coordinated sites, whereas gallium occupies the four-fold and five-fold sites of these two phases, respectively. These results show that the presence of two lattice sites facilitates alloying even in materials that have very different ground state structures because the preferential coordination environment of each component is satisfied, which reduces the energetic destabilization upon mixing.

Multicomponent alloys exhibit configurational disorder (i.e., many distinct possible arrangements of the substitutional atoms over the various lattice sites). Therefore, numerically efficient algorithms are employed here to rapidly examine configurational space. To that end, First-principles based cluster expansion models (CE) are often used to understand the *ab initio* thermodynamics of crystalline mixtures. It provides an efficient and accurate way to compute the relative stabilities of the configurational states within a parent lattice by reducing the energies computed at a higher-level of theory (e.g., DFT) onto a finite set of pair and many-body interactions. This in turn allows for the computation of phase diagrams and prediction of novel ground states. The CE model can be combined with fast stochastic (Monte Carlo) optimization algorithms to identify the lowest energy configuration at a given composition, which allows a rigorous examination of the range of stabilities in a given mixture as a function of concentration.

For the lowest-energy phases at $T = 0$ K, three minima are observed: $x = 0$ (β-phase), $x = 0.5$ (h-phase), and $x = 1.0$ (c-phase). These points are the only structures on the convex hull for $T = 0$ K. At all intermediate compositions, the negative curvature of the energy curve predicts unstable mixtures and phase separation into these minimum energy structures. In the range $0.0 < x < 0.5$, this corresponds to separation into β-Ga_2O_3 and h-$InGaO_3$ ($x = 0.5$), while in the indium-rich regime ($0.5 < x < 1.0$) a separation into h-$InGaO_3$ ($x = 0.5$) and c-In_2O_3 is predicted. Because of these particular shapes of the formation energy curves, a transition between the lowest energy phases occurs at two critical compositions: between the β-phase and the h-phase occurs at $x = 0.4$ and between the h-phase and the c-phase at $x = 0.625$ (see Figure 2).
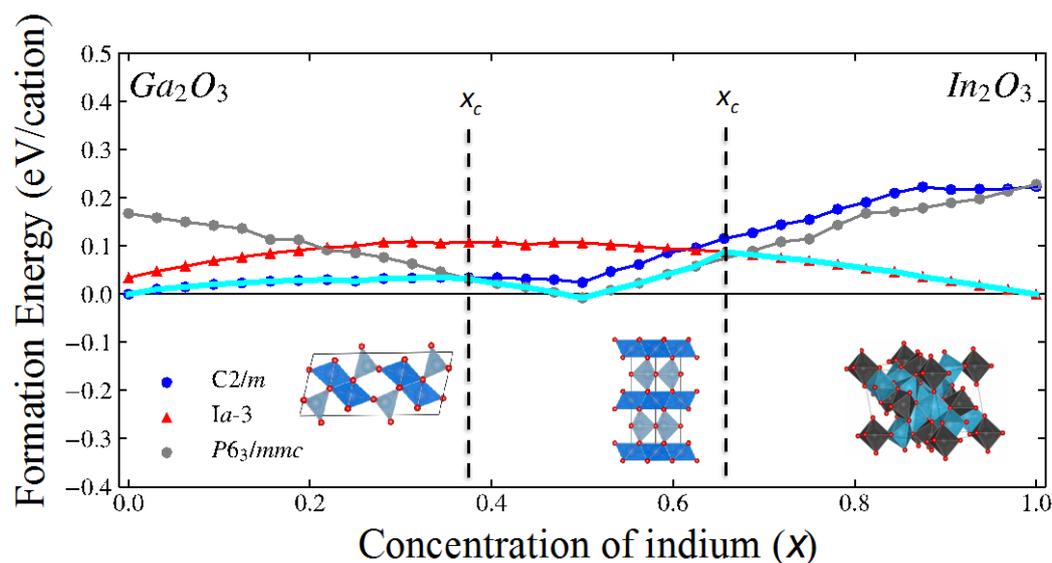
Figure 2. Lowest energy configurations at each composition in the range of x = 0.0 − 1.0 of the three lowest energy phases computed with the PBEsol DFT functional. The critical compositions corresponding to the intersection between two phases is labeled according to the intersections of the lowest energy phases.

These results suggest that the strong preference of In^{+3} in the six-fold coordination environment determines the evolution of the formation energy as a function of increasing indium concentration for the binary phase diagrams of the β and h lattices. To further understand the relationship between the coordination number and formation energy, the mean effective coordination number (ECN) for each cation position in the unit cell is examined (Figure 3). The ECNs are obtained through a weighted sum of the cation-oxygen and cation-cation bond distances, which allows for a continuous coordination number to be generated for each atom self-consistently. In this analysis, sets of ECN values are generated for each cation site in each configuration and then averaged separately for gallium and indium for each structure (Figure 3). Therefore, this metric gives an indication of how the total number of indium or gallium atoms is distributed over these two lattice sites. In this analysis, the ECN values are computed for 100 randomly generated configurations at a concentration of x = 0.5 for the β, c, and h phases. For the β-$InGaO_3$ and h-$GaInO_3$ phases, a lower formation energy is observed for the configurations that have an average indium ECN value close to 6 (i.e., all indium atoms occupy the six-fold coordinated site) with an increase in the formation energy as the ECN values decreases to 4 or 5 (i.e., all occupy the four-fold or five-fold coordinated site). For the c-$InGaO_3$ phase, the average ECN values consistently range from 5.6−6.0 for the 100 configurations because the cubic structure contains only six-fold coordinated cation lattice sites. Therefore, these results indicate that the relative phase stability for $(In_xGa_{1-x})_2O_3$ is strongly determined by the coordination environment of indium.

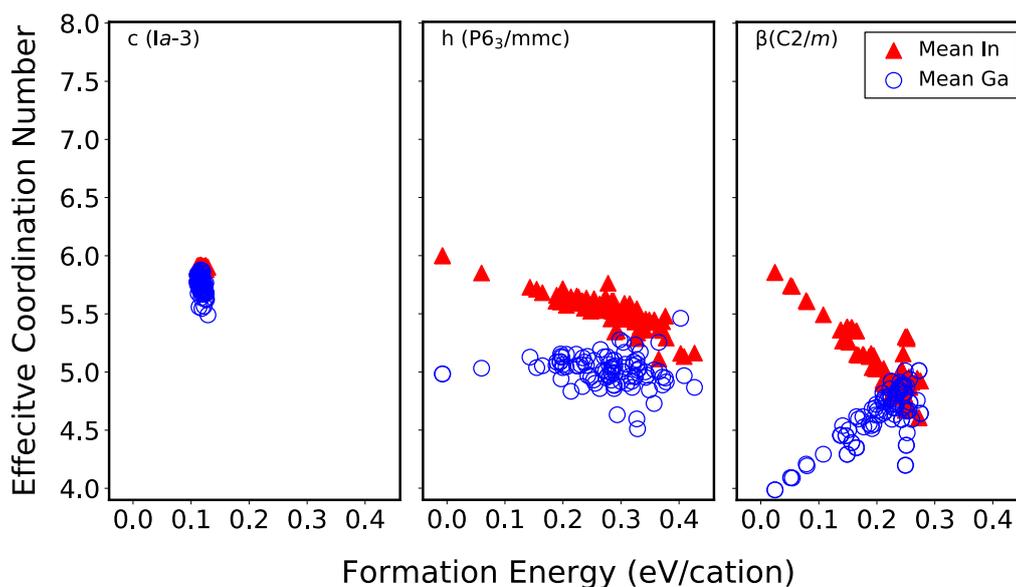*Figure 3. Mean effective coordination number and corresponding formation energies for 100 randomly chosen structures for c-InGaO₃ (left), h-InGaO₃ (middle), and β-InGaO₃ (right).*

The computational results reported here are compared with experiments on films grown by pulsed laser deposition, which are analyzed by high-resolution transmission electron microscopy to resolve the atomic ordering and determine the coordination environment of the gallium and indium atoms in the various phases. The experimental phase stabilities of the ternary $(In_xGa_{1-x})_2O_3$ alloy were investigated for a thin layer with a laterally varying indium content between $0.0 < x < 0.9$, grown at a temperature of 953 K and oxygen pressure of $p(O_2)=10^{-4}$ mbar. The local amount of indium in the various phases in this sample are quantified by scanning electron microscopy energy dispersive X-ray spectroscopy (STEM-EDXS). This measurement indicates that the amount of indium does not exceed $x = 0.50$ for the $\beta-(In_xGa_{1-x})_2O_3$ phase. This agrees well with the fact that at higher indium concentrations the indium has to occupy the tetrahedral lattice sites, which is strongly energetically unfavorable. The indium content in the $h-(In_xGa_{1-x})_2O_3$ phase varies in the range of $x = 0.65$-0.70, which is slightly higher than expected from the calculations. In the cubic $(In_xGa_{1-x})_2O_3$ phase, gallium concentrations up to ca. 10% (i.e., $x = 0.9$) are observed, exactly as the calculations predict.

STEM images recorded with a high-angle annular dark-field detector (HAADF) are examined for samples of β-, h-, and $c-(In_xGa_{1-x})_2O_3$ alloys with indium concentrations of approximately $x = 0.4, 0.6$ and 0.9, respectively (Figure 4). Individual four/five/six-fold coordinated cation columns have been identified by comparing the high-resolution image pattern with stick-and-ball-models of the respective phases. The intensity line profiles shown at the bottom are averages of multiple line-scans extracted along two differently coordinated cation columns for the β- and h-phases. Since $I \sim Z^2$, the higher intensity observed on the six-fold lattice site (pink) indicates in both cases a preferential incorporation of the heavier indium atoms into this position. The gallium atoms on the other hand are mostly observed in the four-fold and five-fold cation positions of the β- and h-phase, respectively. In contrast, all cation lattice sites have the same six-fold environment in $c-(In_xGa_{1-x})_2O_3$, and therefore, only slight intensity variations are observed due to the statistical incorporation of the gallium atoms. These results indicate that the occupation of the lattice sites by indium and gallium is consistent between the various phases irrespective of the composition in terms of the specific coordination environments. They also provide experimental evidence for the strong energetic preference of In^{3+} for an octahedral coordination environment, which was evident in the ECN analysis of various configurations of the β-, h-, and c-phases.
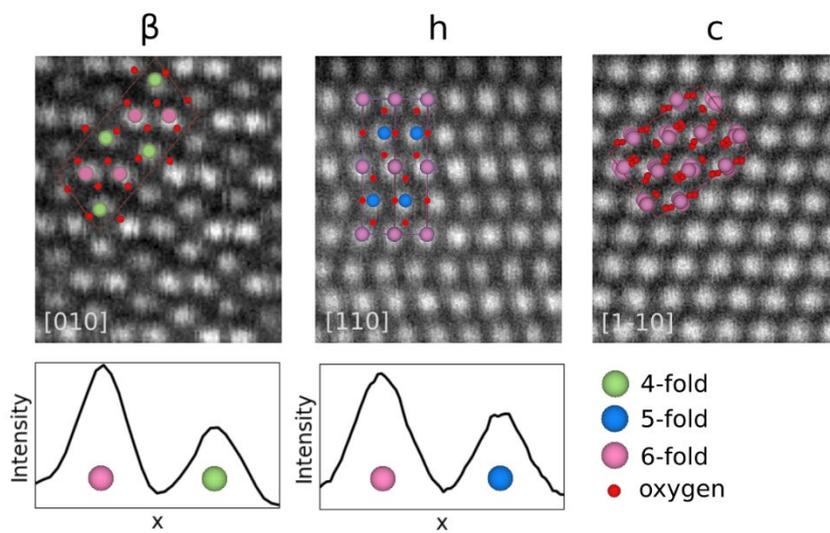
Figure 4. Experimental high-magnification STEM-HAADF images (several images summed to enhance contrast) of the β-, h-, and c-$(In_xGa_{1-x})_2O_3$ alloys with overlay of the stick-and-ball models of one unit cell. The lower plots show HAADF intensity line profiles from the STEM images along the two differently coordinated atoms in the β and h lattices.