Synthesis and Crystal Structures of $InGaO_3(ZnO)_m$ (m = 2 and 3)

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ZnO has unique optical, electronic and piezoelectric properties and is therefore used for various applications such as phosphors, varistors and mechanical transducers. The reaction of ZnO with oxides of trivalent ions (sesqui oxides) leads to compounds with unusual structural characteristics and improved properties for electronic or thermoelectric applications. The general formula of such mixed oxides is $ARO_3(ZnO)_m$ (m = integer; A, R = trivalent ions). Several homologous compounds of oxides of $ARO_3(MO)_m$ (M = Mg, Mn, Fe, Co, Cu, Zn, Cd; A = Sc, Y, In, Ho, Er, Tm, Yb, Lu; R = Al, Fe, Ga) are described [1], mostly by TEM methods. Aristotypes for this series of compounds are $YbFe_2O_4$ (=$FeYbO_3(FeO)_1$) [2] and In_2ZnS_4 (=$In_2S_3(ZnS)_1$) [3].

An optimized high temperature route in sealed platinum tubes was used for synthesis of pure powders of members of the homologues series $InGaO_3(ZnO)_m$. Single crystals of $InGaO_3(ZnO)_2$ were grown from a K_2MoO_4 flux. $InGaO_3(ZnO)_2$ crystallises in the hexagonal crystal system ($P6_3/mmc$; No. 194), deduced from convergent beam electron diffraction (CBED) [4]. Single crystal structure refinement from XRD data (a = 3.2909(2) Å; c = 22.485(2) Å; Z = 2; 1603 data, $R1$ = 0.0237) revealed a compound which consists of an alternate stacking of $\left[InO^{-}_{6/3}\right]^{\infty}_{2}$ and $\left[(Ga,Zn)O^{+}_{4/4}\right]^{\infty}_{3}$ corresponding to CdI_2 and wurtzite type structure motifs, respectively. Inversions of the ZnO_4 tetrahedra occurs (i) at the InO_6 octahedral layer and (ii) halfway in the wurtzite type region, where the inversion boundary is built by Ga^{3+} in trigonal bipyramidal coordination with a long Ga-O_{apical} distance of 2.138 Å. The site occupation of Zn^{2+} and Ga^{3+}, respectively, was confirmed by valence sum calculations. The structure of $InGaO_3(ZnO)_3$ was refined from powder X-ray diffraction data.

$InGaO_3(ZnO)_3$ crystallises trigonal ($R\bar{3}m$; No. 166; a = 3.2871(9) Å; c = 41.589(1) Å, R_{Bragg} = 0.0506). The space group was confirmed by CBED [4]. The structure of $InGaO_3(ZnO)_3$ is similar to $InGaO_3(ZnO)_2$, however, the wurtzite type part of the structure has an even number of closed packed oxygen layers and thus the inversion boundary within this area is different. The compounds described here have the structural charactistics as other known members [1, 5] with general formula $(ARO_3)\cdot(ZnO)_m$) with m = integer.

Currently, pure compounds of members of the $InGaO_3(ZnO)_m$ family with m > 3 are being prepared in our laboratory. In future work, the structures from single crystal data in combination with CBED and bond valence calculations shall be determined with focus on the cation distribution within the $(Zn,Ga)O_4$ tetrahedra. In compounds with large m a different type of ordering and even formation of the unavoidable inversion boundary is expected [6, 7].

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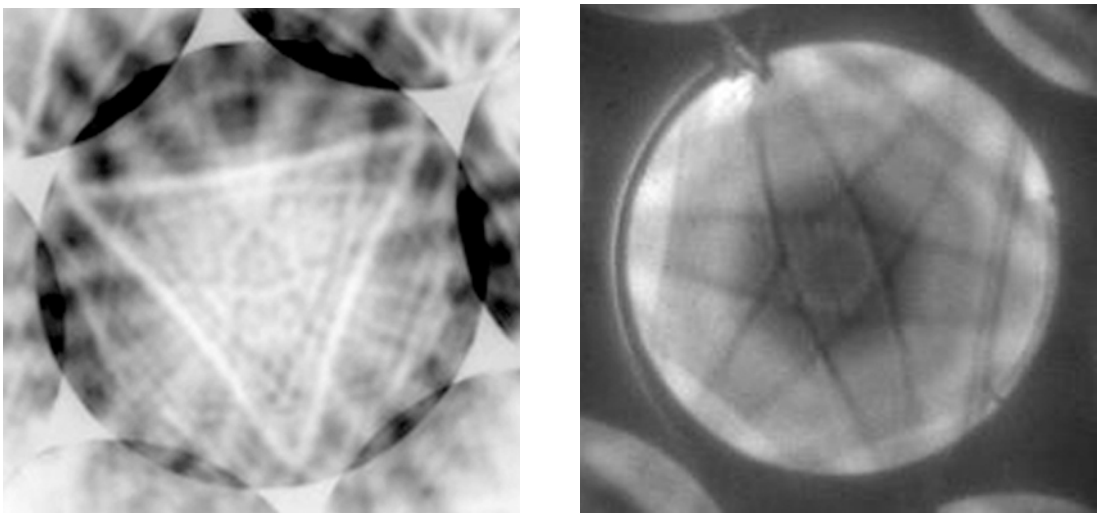

Figure 1. Convergent beam electron diffraction patterns (CBED) from the central discs of $InGaO_3(ZnO)_3$ (left) and $InGaO_3(ZnO)_2$ (right) along <0001>. Data acquired with Gatan GIF mounted on a Philips CM300 FEG UT .

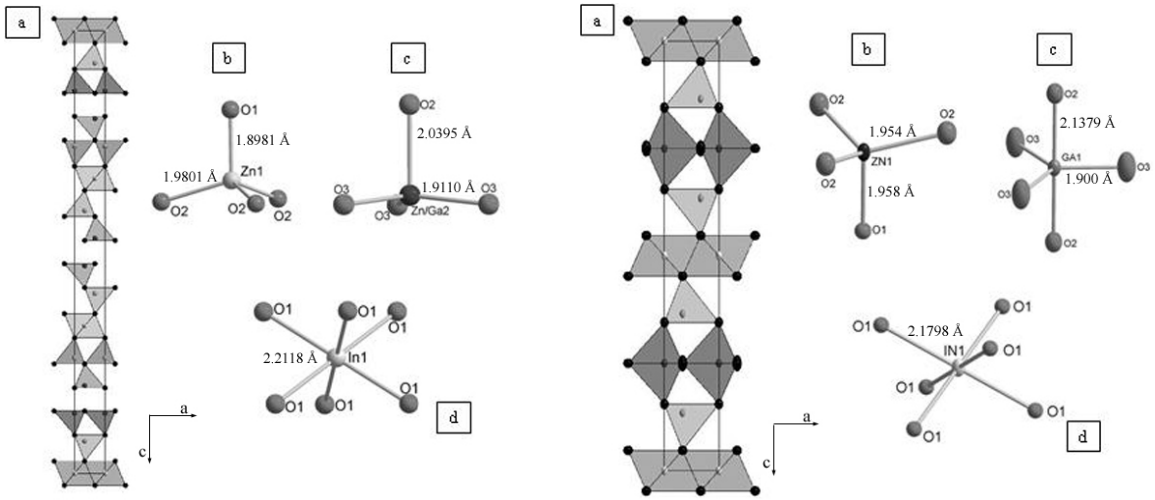

Figure 2. Structure of $InGaO_3(ZnO)_3$ (left) viewed along *b* (a). Coordination of Zn^{2+} (b), Zn^{2+}/Ga^{3+} (c), and In^{3+} (d). Structure of $InGaO_3(ZnO)_2$ (right) viewed along *b* (a). Coordination of Zn^{2+} (b), Ga^{3+} (c), and In^{3+} (d) with thermal displacement parameters at 90 % probability.

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