Homologous compounds of type $ARO_3(ZnO)_m$ in the system Ga-Sn-Zn-OSimon Eichhorn^a, Herbert Schmid^b, Wilfried Assenmacher^a, Werner Mader^{a,*}^a Institute for Inorganic Chemistry, University of Bonn, Roemerstr. 164, Bonn 53117, Germany^b Max Planck Institute for Solid State Research, Heisenbergstr. 1, Stuttgart 70569, Germany

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ABSTRACT

Several members of hitherto unknown homologous compounds $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_m$ ($m=3-7$) of the general formula $ARO_3(ZnO)_m$ were prepared by solid state methods from the binary oxides in sealed Pt-tubes. UV–vis measurements confirm these compounds to be transparent oxides with an optical band gap in the UV region with $E_g \approx 3$ eV. Rietveld refinements on powder samples of $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_m$ proved the compounds to be isostructural with $InGaO_3(ZnO)_m$, where In^{3+} on octahedral sites is replaced statistically by Sn^{4+} and Zn^{2+} in equal amounts preserving an average charge of 3+. Additionally, the structure of $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_3$ has been determined from flux-grown single crystals by X-ray diffraction ($R\bar{3}m$, $Z=3$, $a=3.2387(7)$ Å, $c=41.78(1)$ Å, 19 parameters, 201 independent reflections, $RI=0.047$, $wR2=0.074$). The compound $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_3$ is isostructural with $InGaO_3(ZnO)_3$. $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_3$ was furthermore analyzed by High Angle Annular Dark Field (HAADF) scanning TEM and EELS spectroscopic imaging, supporting the structure model derived from X-ray diffraction data.

1. Introduction

Transparent semiconducting oxides gain increasing attention because of their promising properties that make them candidates for electronic applications like flat and touch panel displays or thin film solar cell contacts. A range of In-Ga-Zn-O compounds summarized as IGZO has been commercialized for thin film transistor (TFT) fabrication after in 2003 Nomura et al. [1] realized $InGaO_3(ZnO)_5$ to have impressive effective mobility of $80 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, turn-on voltage of -0.5 V and on/off ratio of 10^6 . Similar results were published for Sn-Ga-Zn-O TFTs by Ogo et al. in 2008 [2] or more recently by Nguyen et al. [3]. The bottom of the conduction band of the ionic oxide semiconductor IGZO is composed of highly isotropic, overlapping 5 s orbitals of indium [4], resulting in higher carrier mobilities in comparison to the covalent amorphous semiconductor a-Si. Isostructural Sn-Ga-Zn-O materials might share these advantageous properties because Sn^{4+} has the same electron configuration ($4d^{10}$) as In^{3+} . However, besides the binary oxides only the spinel type oxides $ZnGa_2O_4$, $SnZn_2O_4$ and their solid solution are known to exist in the system Sn-Ga-Zn-O at 1250 °C according to Palmer et al. [5].

The IGZO compounds are members of the homologous series $InGaO_3(ZnO)_m$ ($m = \text{integer}$) of general type $ARO_3(ZnO)_m$ in which layers of edge sharing octahedra $[AO_{6/3}]^-$ (large A^{3+} ion) and wurtzite type regions of variable size $[RO(ZnO)_m]^+$ (small R^{3+} ion) are alternately stacked along the c -axis [6–9]. $InGaO_3(ZnO)_m$ ($m=1-13$) phases

were first synthesized by Nakamura et al. [10] and Kimizuka et al. [11] by solid state reactions. In a recent paper [12] we presented new layered compounds $[In_{1-2x}Sn_xZn_x]GaO_3(ZnO)_m$ ($m=1, 2$) where In^{3+} is aliovalently substituted by Sn^{4+} and Zn^{2+} in equal amounts. Complete substitution of In^{3+} is not possible in the compounds with $m=1$ and 2; $[In_{0.16}Sn_{0.42}Zn_{0.42}]GaO_3(ZnO)_2$ represents the compound with highest substitution.

In this contribution we successfully synthesized fully substituted compounds $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_m$ ($m=3-7$) by solid state methods. Lattice parameters and crystal symmetry are determined by X-ray powder diffraction and electron diffraction in principal zone axes. The Rietveld refinement of powder diffraction data proves the oxides to have the structure of $ARO_3(ZnO)_m$ homologous compounds. Single crystals of $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_3$ were grown for detailed X-ray structure analysis and compound is characterized by high angle annular dark field (HAADF) STEM and electron energy loss spectroscopy (EELS) methods. The optical properties are measured by UV–vis spectroscopy.

2. Experimental details

Powders of $[Sn_{0.5}Zn_{0.5}]GaO_3(ZnO)_m$ were synthesized from ZnO (99.9% cation basis, Sigma Aldrich), Ga_2O_3 (99.999% cation basis, Alfa Aesar) and SnO_2 (99.99% cation basis, Sigma Aldrich) as starting materials. Polycrystalline powders were synthesized by ceramic meth-

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ods at temperatures between 1200 °C and 1450 °C in sealed platinum tubes to prevent evaporation of metal oxides. Samples were thoroughly ground under acetone in an agate mortar and uniaxially pressed to 13 mm pellets under a weight of eight tons. The platinum tubes were annealed for 48 h and slowly cooled to room temperature.

Single crystals of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_3$ were grown in sealed Pt-tubes from stoichiometric mixtures of ZnO, Ga_2O_3 and SnO_2 in a flux of K_2MoO_4 (98% cation basis, Sigma Aldrich). The oxides and potassium molybdate were mixed in a 1:10 weight ratio. The flux was annealed at 1300 °C for two days and slowly cooled to 750 °C at a rate of -6 K/h.

Powder X-ray diffraction was used to determine the formation of products and the phase purity. Powder XRD measurements were conducted on a Philips PW 1050 using $\text{Co-K}\alpha$ radiation in Bragg Brentano geometry and equipped with a post specimen monochromator. The lattice parameters were refined by the CelRef [13] software, where additions of silicon were used as internal standard for the correction of the zero point and the displacement error. XRD data were acquired on a STOE IPDS-2T with $\text{Mo-K}\alpha$ radiation at -150 °C.

Electron diffraction and energy dispersive X-ray (EDX) spectroscopy of powders dispersed on carbon coated copper grids were conducted in a FEI-Phillips CM30 transmission electron microscope. High resolution HAADF STEM and EELS spectroscopic imaging were conducted on a probe corrected scanning transmission electron microscope (JEOL JEM-ARM200F) equipped with cold FEG and EELS (Gatan GIF Quantum ERS) and EDXS (Jeol Centurio SDD) spectroscopic attachments. A nonlinear filtering algorithm was used for denoising of HAADF-STEM images [14]. A scanning electron microscope (JEOL JSM-6400F FEG-SEM) equipped with an HPC detector and Voyager (Noran) (EDXS) system was used for imaging and for chemical microanalysis of single crystals.

UV-vis spectra were recorded in reflection mode from a mixture of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$ powders and BaSO_4 as white standard.

3. Results

3.1. Compounds of the homologous series $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$

Several new members of the homologous series $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$ with integer $m=3-7$ have been obtained by reaction of the binary oxides at elevated temperatures. Compounds with $m=3-5$ are pure white powders whereas compounds with $m=6, 7$ are slightly yellow. The chemical compositions, i.e. cation ratios of the compounds, were measured by EDX spectroscopy in a transmission electron microscope and are in very good agreement with the weighted sample and hence with the aimed compound composition (Supporting Information S.I., S20). XRD powder diffraction patterns of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$ are presented in Fig. 1. Lattice parameters as results of cell refinements derived from powder diffraction data are summarized in Table 1.

Furthermore, the profiles of the powder patterns were matched by Rietveld refinements. As starting models served the single crystal structure data of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_3$ and literature data [7,22,33] of supposed isostructural compounds for the members of the $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$ series with $m > 3$.

The results prove the oxides to have the structure of $\text{ARO}_3(\text{ZnO})_m$ homologous compounds, and that the powder samples have very little impurities only. Moreover, atom positions of all members of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$ ($m=3-7$) could be obtained as refinement results. The Rietveld refinements showed a strong preferred orientation along [0001] for every compound, which is caused by a combination the plate-like shape of the crystals and the Bragg-Brentano-geometry of the diffractometer. The site occupation factor (sof) of the mixed occupied octahedral site could be refined and resulted in reasonable occupation factors for Zn^{2+} and Sn^{4+} close to 0.5. This indicated the presence of Sn and Zn on this site, but for reasons of charge balance, this sof was fixed to 0.5. Details of the refinement, crystal data, atomic

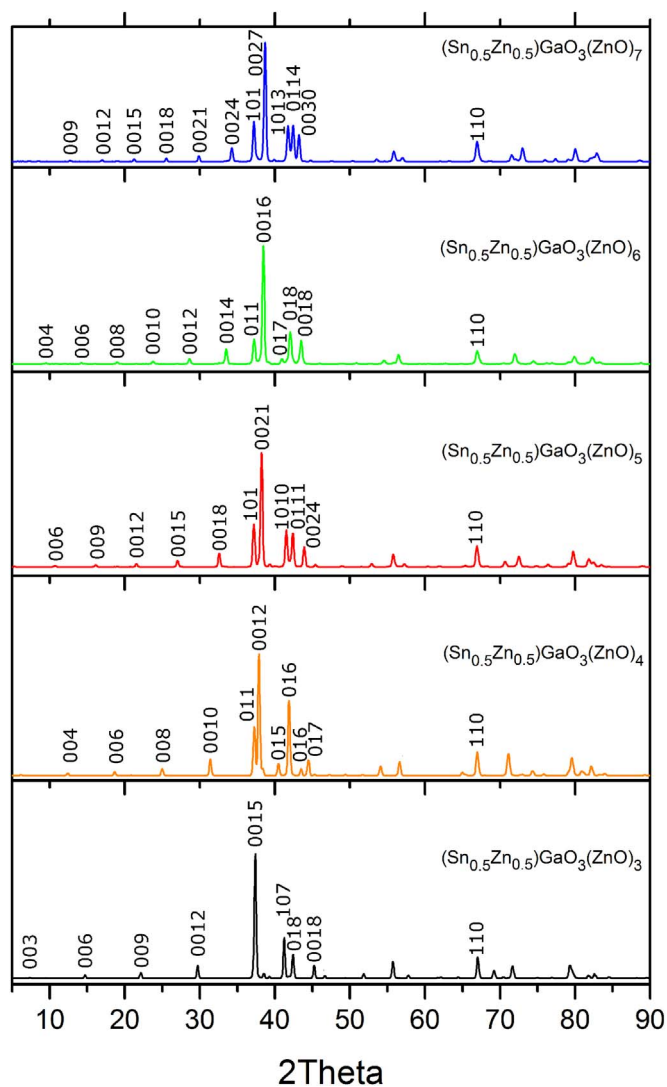


Fig. 1. X-ray Powder diffraction patterns of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$ ($m=3-7$) with decreasing m from top to bottom. Diffraction patterns prove single phase products.

Table 1

Lattice constants of oxides $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_m$ with integer $m=3-7$.

	Space Group	a [Å]	c [Å]
$[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_3$	$R\bar{3}m$	3.244(2)	42.0102(3)
$[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_4$	$P6_3/mmc$	3.2460(8)	33.1164(1)
$[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_5$	$R\bar{3}m$	3.2475(5)	57.4564(1)
$[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_6$	$P6_3/mmc$	3.247(2)	43.4932(1)
$[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_7$	$R\bar{3}m$	3.2482(8)	73.1149(1)

parameters and structure figures are given in the S.I. S9–S19.

3.2. Crystal structure of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_3$

Selected area electron diffraction (SAED) patterns of $[\text{Sn}_{0.5}\text{Zn}_{0.5}]\text{GaO}_3(\text{ZnO})_3$ crystals in three principal zone axes are shown in Fig. 2. The diffraction patterns are indexed using the hexagonal Miller-Bravais notation $hkil$. In [0001] orientation diffraction pattern reflections from a higher order laue zone (HOLZ) can be observed with low intensity. Evaluation of the reflection conditions yields hkl : $-h + k + l = 3n$, $h + l = 3n$, $l = 3n$, and $000l$: $l = 3n$ which are in agreement with the two space groups $R\bar{3}m$ and $R\bar{3}m$.

A hexagonal plate-shaped, colorless crystal of ca. $10 \times 10 \times 5$ μm was

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