The (Zn^{2+}, Ga^{3+})-Partition Investigation of the Homologous Series $Ga_2O_3(ZnO)_m$ ($m=9$ and 10) Applying the Bond Valence Model

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Abstract—**The (Zn^{2+}, Ga^{3+})-partitions of the homologous series $Ga_2O_3(ZnO)_m$ (m=9 and 10) are investigated with the high energy synchrotron single crystal X-ray diffraction data, collected with the wavelength, λ =0.47Å, in sufficient distance of the Zinc and Gallium-K-absorption edge, where the resonant scattering effect is greatly small. The synthesized single crystals of $Ga_2O_3(ZnO)_9$ and $Ga_2O_3(ZnO)_{10}$ crystallize in the space group Cmcm with cells parameters a=3.252(5), b=19.695(5), c=33.589(4) and a=3.252(5), b=19.958(5), c=36,541(2)Å, and $\alpha=\beta=\gamma= 90°$ respectively. The structures consist of parts of known oxide structures with the apparition of split-position on the mirror plan. Zn^{2+}- and Ga^{3+}-partitions are determined applying the bond valence theory. The result reveals over the unit cell modulated variations of Zinc and Gallium concentration.**

Keywords— Bond Valence; Bond Strength; Cation Partitions; Homologous Series

INTRODUCTION

Pure Zinc oxide is a n-type semiconductor with a band gap of 3.37 eV and a specific resistance of about 300Ω.cm. Doped with trivalent metal ions, the specific resistance can be considerably enhanced [1,2]. The homologous series arise from the doping of the ZnO with an exceeding amount of trivalent metal ions, which can replace the divalent Zn ion but cannot retain the wurtzite structure [3]. Since the ZnO materials are candidates for photocatalysts, transparent conducting oxides and thermoelectric materials and also the most useful material in the manufacture of different devices such as ultrasonic signal converters, oxygen sensors and chemical sensors, the homologous phases $In_2O_3(ZnO)_m$ and related compounds have been extensively investigated [4, 5, 6]. In addition, the structural examination revealed that the structures of $Fe_2O_3(ZnO)_m$ are the superstructures of $In_2O_3(ZnO)_m$ [7, 8]. High resolution microscopy and single crystal X-ray studies showed that the structure of $Ga_2O_3(ZnO)_m$ is fundamentally different from that of $In_2O_3(ZnO)_m$ type [9,10]. Recently, an unified description for structures in the serie $Ga_2O_3(ZnO)_m$ was presented using

the (3+1)-dimensional superspace description, in which the structures were treated as commensurate phases of the compositely modulated structures [11,12]. Moreover, the homologous series, $(Ga_2O_3)_2(ZnO)_{2n+1}$ derived from the conventional method in three dimensional space of $(Ga_2O_3)_2(ZnO)_{13}$ and in spite of their best endeavor, the (Zn^{2+}, Ga^{3+})-partitions exactly were impossible to calculate [13]. The new member of homologous series $Ga_2O_3(ZnO)_{10}$ has been synthesized and the symmetry was investigated utilizing the convergent beam electron diffraction [14]. Furthermore, structure and (Zn^{2+}, Ga^{3+})-partitions of two members of homologous series, $Ga_2O_3(ZnO)_m$ (m=9, 10), were determined by the means of resonant scattering effect [15].

The understanding of the chemical and physical properties of crystals and their manifold uses in the manufacture of ceramics, catalysts and electrical devices are to be improved if the working knowledge of the bonded interactions at the atomic level has been realized. Bond valence theory is pictured as a very simple form of molecular orbital theory, parameterized by the means of the interatomic distance [16, 17]. Therefore, bond valence provides a reliability check of the correctness of a structure. Likewise, calculations of bond valence strength from the average bond length, $<R(M-O)>$, have been performed in order to accurately investigate the (Zn^{2+}, Ga^{3+})-partitions.

I. EXPERIMENTAL

Metal oxide powder in molar ratios ZnO : Ga_2O_3 = 1 : 9 and 1 : 10 (Sigma Aldrich, 99.99%), were mixed in a ball milling with ethanol. The samples were dried and sealed in a Pt tube and put into a muffle furnace at 873 K. The temperature was automatically increased with a heating rate of 278 K/min until the annealing temperature of 1632 K has been reached. The samples stand in the furnace for 2 weeks. Thereafter, they were slowly cooled and taken out of the furnace at 773 K. Further cooling follows at room

temperature. As outcomes, light yellow to yellow metallically shining dense single crystals were synthesized. Single crystals are mounted on automatic four circles point detector diffractometer at the radiation line D3 of Hamburger Synchrotron Labs (SMART, Fa BRUKER). Diffraction data have been collected with the wavelength, λ =0.47Å, in sufficient distance of the Zinc and Gallium-K-absorption edge, where the resonant scattering effect is negligible. By contrast, in our recent work data have been collected with the wavelength, λ =1.285Å, near the K-absorption edge of Zn [15]. Reflection intensities have been integrated using the program XDS version 06/2007 and for data reduction the program SORTAV has been further used. Owing to the isoelectronic feature of Zn^{2+} and Ga^{3+} the crystal structures have been at first solved by the means of Sir98 by assuming that there is only Zn in the structure. Thus, the structure refinements follow with the program SHELX97 [18] are based on the assumption that all metal sites can be occupied by Zn and Ga at the same time. Correspondingly, equal fractional atom site coordinates and square atomic displacement parameters have been ascribed to Zinc and Gallium atoms. The dispersion correction has been subtracted from Sasaki [19].

According to the Pauling's bond valence model, the sum of the average bond strengths $\langle s \rangle$ (valence of the metal atom/coordination number) to each anion in a stable material was postulated to exactly or nearly equal the negative valency on the anion $\sum_{anion} \langle s \rangle \cong -Q_{anion}$ [20, 21, 22, 23, 24].

Bond valence-bond length relation for bonds between oxygen and many of metal atoms were derived and can be exhibited with the power law like expression: $s = \left(R(M-O)/R_o \right)^{-N}$ where s was defined to be the empirical bond valence for a given M-O bonded interaction and Ro and N can be viewed as lagrangian multipliers obtained with the side constraint that the sum of bond valences reaching each of the metal and oxygen atoms in a structure matches the nominal bond valence of the atoms [16]. Since the parameters Ro and N are independent of the ionic character and the coordination number of metal atoms, all ions with isoelectronic cores can be distinguished [25]. Previous researches have revealed that the average bond lengths $<R(M-O)>$ are connected with the mean bond valence s and the row number r of periodic table of element by the power law expression : $\langle R(M-O) \rangle = fac \left(\langle s \rangle / r \right)^{-0.22}$

Where the empiric best value fac=1.39 can slightly vary for a given amount of M-O bond length [16, 17, 26]. From the calculating bond strength, attempts have been made in order to determine the partition Zn and Ga in term of concentration, based on the assumption that the sum of bond strengths of all cation sites is equal the sum of charges $\sum \langle s_{ic} \rangle = \sum Q_c$. This means for the present compounds that the bond valence was adjusted by the variation of fac to $\sum Q_c = 24$ and $\sum Q_c = 26$ for Ga$_2$O$_3$(ZnO)$_9$ and Ga$_2$O$_3$(ZnO)$_{10}$, respectively. The definite site occupancy through Zn can be assessed from the sum of bond strength and averaged bond lengths available. As it depends on whether this c-th site is exclusively occupied by Ga^{3+} or Zn^{2+}, the average bond strength $\langle s_{ic} \rangle$ for c-th site could be equal 2 or 3 for Zn^{2+} or Ga^{3+} . The equality $[Zn]_{c-th} = 3 - \langle s_{ic} \rangle$ determines the Zn concentration on the c-th cation sites.

II. RESULTS

The bond valence model has been applied from the collected data on single crystals of maximal size 360x100x20μm. Crystallographic data, experimental condition for data collection and refinement are listed in Table1. Projections of the structures for both compounds along [100] are given in Figure 1. The structures of Ga$_2$O$_3$(ZnO)$_9$ points out seven tetrahedral coordinated sites M01, M03, M04, M05, M06, M07 and M08 which form wurtzit-like partial structure, five trigonal-bipyramidal coordinated sites M09, M10, M11, M12 and M13 and a square-pyramidal coordinated site M02. The trigonal-bipyramidal coordinated sites lie between the mirror plan $\mathbf{m_z}$ and form ladder-like partial structure as in the ß-Ga$_2$O$_3$ appears. The mirror plan contains a split position which is described by M02 and M03. Instead of five trigonal-bipyramidal coordinated sites as mentioned above the compound Ga$_2$O$_3$(ZnO)$_{10}$ points out six trigonal-bipyramidal coordinated sites from M09 to M14, seven tetrahedral coordinated sites M01 and M03 to M08, which form wurtzit-like partial structure and a square-pyramidal coordinated site M02 as mentioned in our recent research [15].

Zinc and Gallium are ionic isoelectronic and share the same cation site. Therefore, the position parameter and square atomic displacement parameters have been set equal for each cation site. Based on calculated average bond strength and cation distribution in terms of concentration, the site M01 possess only Zn; Ga and Zn simultaneous occupy both split-positions with high Zn concentration on M02 and high Ga concentration on M03. The tetrahedral coordinated sites, M04, M05, M06, M07 and M08, possess high Zn concentration and the trigonal-bipyramidal coordinated sites, M09, M10, M11, M12 and M13, high Ga concentration. The averaged bond lengths with the corresponding bond strength and the Zn concentrations on each cation sites are listed in Table 2. The graphical representations of Gallium concentration against $\mathbf{z}$-coordinate of asymmetric unit cell show that the Gallium concentration decreases from the ladder structure part to the wurtzit structure part (Figure 2).

Table 1: crystallographic data, condition for data collection and refinement for $Ga_2O_3(ZnO)_9$ and $Ga_2O_3(ZnO)_{10}$

Crystal data		
Chemical formula	$Ga_2Zn_9O_{12.}$	$Ga_2Zn_{10}O_{13.}$
Mw(g/Mol)	7358.16	8009.12
Crystal system, space group	Orthorhombic, Cmcm	Orthorhombic, Cmcm
a, b, c (Å)	3.252(5), 19.695(5), 33.589(4)	3.252(5), 19.958(5), 36.541(2)
$\alpha= \beta= \gamma$ (°)	90	90
V (Å³)	2151.31	2367.05
Z	8	8
D_x (kg.m^{-3})	5.679	5.619
$\mu_{\lambda=0.47}$ (mm^{-1})	12.93	12.79
$\mu_{\lambda=1.285}$ (mm^{-1})	27.67	27.45
F(000) (e)	3424	3728.0
Crystal size (µm)	360x100x20	140x40x10
Data collection		
Diffractometer	Four-cycle	Four-cycle
Monocromator	Si(111) double crystal	Si(111) double crystal
Monitor	polarimeter	polarimeter
λ (Å)	0.47	0.47
s_{max} (Å^{-1})	0.991	0.992
θ_{max}	49.99	55.61
Range of h, k, l	h = 0→5, k= 0→34, l = l→60	h =-6→ 6, k =0→68, l =0→ 19
Scan method	ω-2θ	ω-2θ
$\Delta\omega$	0.025	0.025
Number of measured and unique reflections	8759, 1993	9348, 2238
Refinement		
R, R$_w$, GOF	0.021, 0.050, 1.093	0.028, 0.082, 1.047
Number of parameters	148	168
Number of restraint for λ	0	0
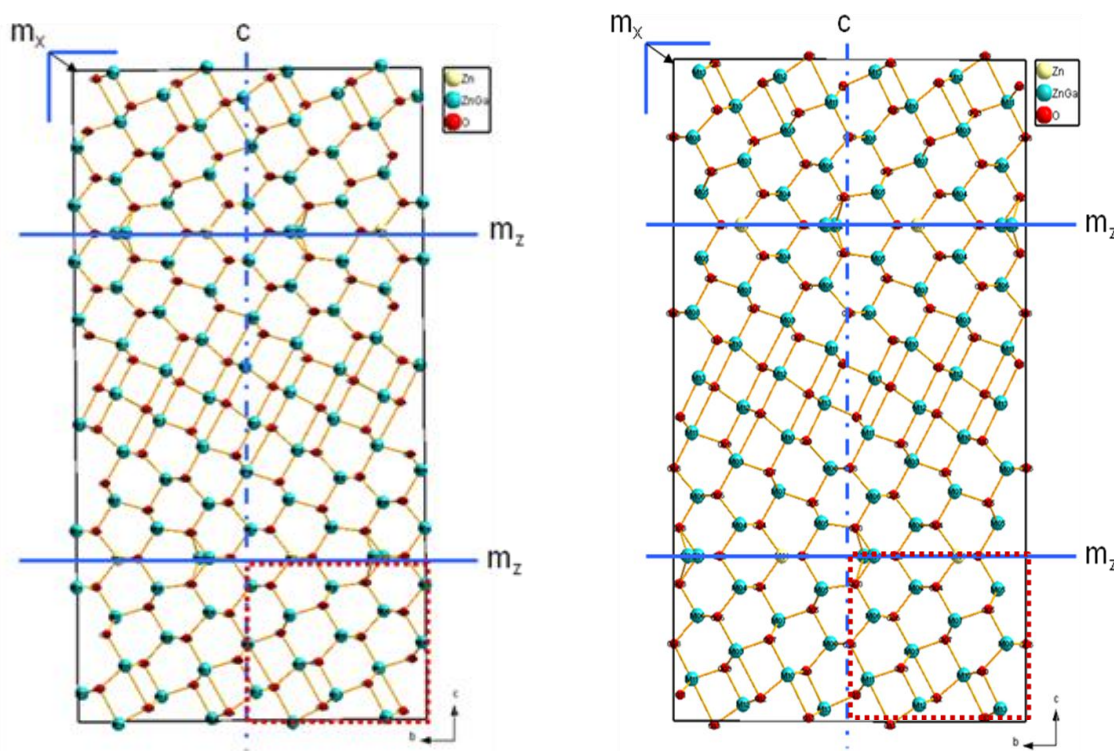
Figure 1. detailed projection of the structure model for $Ga_2O_3(ZnO)_{10}$

(left) and $Ga_2O_3(ZnO)_9$ (right) along a-axis, m_z and m_x are mirror plans and c is the sliding mirror plan(the red squares on both structures illustrate the asymmetric unit cell).

Table 2: averaged M-O Bond length (Å), corresponding average bond strength, and calculated Zinc- and Gallium-Concentration(%) of $Ga_2O_3(ZnO)_9$ and $Ga_2O_3(ZnO)_{10}$ respectively

|		$\langle s_{ic} \rangle$	[Zn]	[Ga]		$\langle s_{ic} \rangle$	[Zn]	[Ga]
<R(M01-O)>	1.991	1.96	1.04	0	1.998	1.95	1.05	0
<R(M02-O)>	2.124	2.04	0.96	0.04	2.132	2.04	0.96	0.04
<R(M03-O)>	1.894	2.62	0.38	0.62	1.902	2.58	0.42	0.58
<R(M04-O)>	1.965	2.08	0.92	0.08	1.975	2.06	0.94	0.06
<R(M05-O)>	1.973	2.05	0.95	0.05	1.983	2.02	0.98	0.02
<R(M06-O)>	1.949	2.16	0.84	0.16	1.957	2.15	0.85	0.15
<R(M07-O)>	1.971	2.05	0.95	0.05	1.977	2.05	0.95	0.05
<R(M08-O)>	1.972	2.05	0.95	0.05	1.984	2.02	0.98	0.02
<R(M09-O)>	2.124	2.19	0.81	0.19	2.151	2.16	0.84	0.16
<R(M10-O)>	2.068	2.27	0.73	0.26	2.123	2.19	0.81	0.19
<R(M11-O)>	2.094	2.27	0.73	0.27	2.131	2.19	0.81	0.19
<R(M12-O)>	2.035	2.37	0.64	0.36	2.047	2.33	0.67	0.33
<R(M13-O)>	2.027	2.40	0.60	0.40	2.064	2.32	0.68	0.32
<R(M14-O)>	-	-	-		2.032	2.39	0.62	0.38
$\sum \langle s_{ic} \rangle = 24$					$\sum \langle s_{ic} \rangle = 26$			
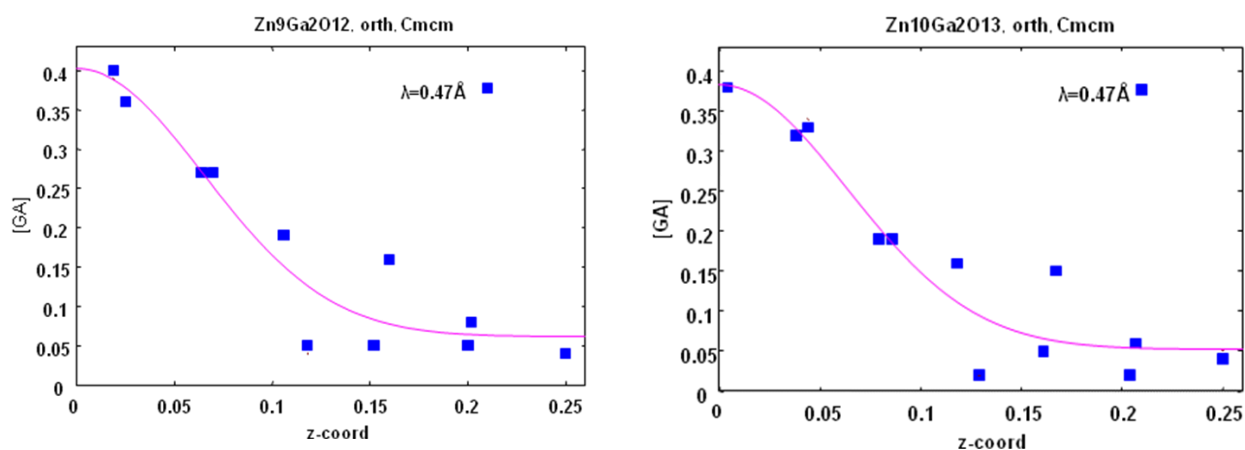
Figure 2: Ga-concentration derived from average bond strengths plotted against z-coordinate extracts from the atom site coordinates for both compounds (asymmetric unit cell).

III. CONCLUDING REMARKS

For determining the Zn^{2+} - and Ga^{3+}- partition from the high resolution synchrotron radiation data, the structure has been solved and refined with the reflections collected in sufficient distance of the Zinc and Gallium-K-absorption edge. After iterative process of refinement, the least square procedure has converged and the refinement of the parameter is completed so that the global measure of fit, the indices R, R_w and the goodness of fit GofF are resulted with the following values 0.021, 0.050 and 1.093 for $Ga_2O_3(ZnO)_9$ and 0.028, 0.082 and 1.047 for $Ga_2O_3(ZnO)_{10}$ respectively. The Pauling´s bond valence model is exploited to calculate the site occupation factor. Zn and Ga unequally share the metal sites from M04 to M14, whereas the polyhedral, M01 and M02, and M03 are occupied by Zn and by Ga respectively. The Gallium concentrations decrease from five-coordination sites to tetrahedral, whereas the coordination numbers increase with the decreasing Zinc concentration. Ga- concentration decreases with z-

coordinate in asymmetric unit cell, and thus modulated variation of Zn- and Ga- concentration in extended unit cell. Since qualitatively similar results for both compounds are found applying the bond valence theory, the calculated metal partitions appear as a structurally characteristic feature which, with some probability, belong to another homologous compounds of type $Ga_2O_3(ZnO)m$. Further studies on homologous compounds are required to distinguish which of the two methods to calculate Zn^{2+}-, Ga^{3+}- partition (bond valence method or resonant scattering effect) is most reliable.

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