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Structure Determination and (Zn^{2+}, Ga^{3+})-Partitions of Homologous Series $Ga_2O_3(ZnO)_m$ (m=9 and 10) Utilizing the Resonant Scattering Effect

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Abstract:- **The structures and (Zn^{2+}, Ga^{3+})-Partitions of $Ga_2O_3(ZnO)_m$ (m=9, 10) are determined by high energy synchrotron single crystal X-ray diffraction technique, with the data collected at the wavelength, λ=1.285Å, near the Zn-K-absorption edge where Zinc and Gallium are possibly discriminated by the change of scattering contrasts. 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 α = β = γ = 90° respectively. The structures consist of parts known oxide structures with the apparition of split-position on the mirror plan. Zn^{2+}- and Ga^{3+}- partitions directly derive from the least square structure refinement. The result reveals over the unit cell a modulated variation of Gallium and Zinc concentration.**

1. INTRODUCTION

Zinc Oxide of the wurtzite structure is the most useful material in the manufacture of different devices such as ultrasonic signal converters, oxygen sensors and chemical sensors [1, 2, 3]. Pure Zinc oxide is an n-type semiconductor with a band gap of 3.37 eV and a specific resistance of about 300Ω.cm. Doped with monovalent or trivalent metal ions, the specific resistance can be considerably influenced [4,5]. 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 [6]. Since the ZnO materials are candidates for photocatalysts, transparent conducting oxides and thermoelectric materials [7, 8], the homologous phases $In_2O_3(ZnO)_m$ and related compounds were extensively studied [9]. Further structural Studies revealed that the structures of $Fe_2O_3(ZnO)_m$ are the superstructures of $In_2O_3(ZnO)_m$ [10]. Furthermore, The homologous phases $InMO_3(ZnO)_m$, which is isostructural with $In_2O_3(ZnO)_m$, were found in systems In_2O_3-M_2O_3-ZnO(M= Fe, Ga, Al) [11]. 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 [12, 13]. Recently, a unified description of $(Ga_2O_3)_2(ZnO)_{2n+1}$ are presented by the means of superspace formalism [14], in which the structures are treated as commensurate phases of the compositely modulated structures [15]. Due to the fact that Al^{3+} possess a too small ion radius in order to occupy the octahedral coordinated site, the synthesis of compounds with chemical compositions $Al_2O_3(ZnO)_m$ has failed (N. Kimizuka et al., 1993, M. Nakamura et al., 1990, 1991, 1993)[10, 16, 17,18]. Previously, the new member of homologous series $Ga_2O_3(ZnO)_{10}$ are synthesized and the symmetry are investigated by the means of convergent beam electron diffraction [19].

Since the conventional X-ray structure analysis cannot distinguish the neighbour atoms in the periodic table of element, single crystals of $Ga_2O_3(ZnO)_9$ and $Ga_2O_3(ZnO)_{10}$ are investigated by the means of high energy synchrotron x ray diffraction technique. Crystallographic data are collected with the wavelength near the K-absorption edge of Zn where the targeted generated scattering contrasts are exploited and from which (Zn^{2+}, Ga^{3+})-Partitions are derived.

2. 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, sealed in a Pt tube and put into the furnace at 873 K. The temperature was automatically increased with a heating rate of 278 K/min until the annealing temperature of 1632 K was 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 process followed at room temperature. After complete cooling the samples were moved from the Pt tube.

The intense continuous spectrum of synchrotron radiation was used in order to provoke exceptionally large anomalous scattering. Intensity data were collected for single crystals mounted on automatic four circles point detector diffractometer at the radiation line D3 of Hamburger Synchrotron Labs (SMART, Fa BRUKER). Reflection intensities were integrated using the program XDS version 06/2007 and for data reduction the program SORTAV was further used. The both programs were carried out at D3-Stations-Software. Owing to the isoelectronic feature of Zn^{2+} and Ga^{3+} the crystal structures were at first solved utilizing Sir98 program under the assumption that there is only Zn in the structure. Thereafter, the structure refinements were performed with the program SHELX97 [20] under the assumption that all metal sites can be occupied by Zn and Ga at the same time. Furthermore, the determination of Zn and Ga ions partition was made on the metal sites according to Zn_xGa_{m-x}, where m is the multiplicity of point site. Therefore, equal coordinates and square atomic displacement parameters were attributed to Zinc and Gallium atoms.

The possibility of selecting the wavelength for synchrotron X-ray diffraction has far-reaching consequences. It can be used to enhance the resonant scattering effect on particular elements containing in the sample, for instance, to solve phase problem in macromolecular work by measuring anomalous dispersion effect [21], or to increase the scattering contrast between neighboring atoms in the periodic table [22]. For investigating the cation partitions, the structure refinement with the data measured at Zn-K-edge are applied, whereby the negative term of the atomic scattering factor $f'(E) = -4.97$ of Zn makes $\left|f_{Zn}(|g|,\lambda)\right|$ of Zn against $\left|f_{Ga}(|g|,\lambda)\right|$ of Ga clearly smaller. Then, this creates a scattering contrast, so that thereby the Zn^{2+}- and Ga^{3+}- partitions can be modeled on the cation sites. Furthermore, the structure factor could be written as:

$$F_\lambda(\vec{g}) = \left\{ \sum_{j=1}^{NAK} \left[p_j \left(f^o_{Zn} + f'_{Zn} + i f''_{Zn} \right) + \left(m_j - p_j \right) \left(f^o_{Ga} + f'_{Ga} + i f''_{Ga} \right) \right] \sum_{k}^{NS} G_{jk} T_{jk} \right\} + F(\vec{g})_{ox}$$

where $F(\vec{g})_{ox}$, NAK, m_j, $G_{jk} = \exp(2\pi i \vec{g}\vec{r}_{jk})$, $T_{jk} = \exp\left[-2\pi^2 \vec{g}^T L_{jk} \vec{g}\right]$ and P_j are the partial structure factor of oxygen part structure, the number of cation positions ik of asymmetric unit cell, the multiplicity of j^{-th} cation sites, the geometric factor of j^{-th} cations after k^{-th} symmetry operations, the temperature factor of j^{-th} cations after k^{-th} symmetry operations and cation occupation through Zn respectively. Since the multiplicity of j^{-th} cation sites, m_j, is known, the refinement allows the determination of P_j and the occupations of cation sites through Zn and Ga.

3. RESULTS

The data are collected with the wavelength at the K-absorption edge of Zn. Crystallographic data, condition for data collection and Refinement are listed in Table1. Since Zinc and Gallium are ionic isoelectronic and share the same cation site, the overall scale factor, the position parameter and the thermal parameters are equated to each cation site. Conversely, the site occupancy, that is, the atomic position is statistically set for several sites. After iterative process of refinement, the least square procedure has converged and the refinement of the parameter is completed. The global measure of fit, the indices R, Rw and the goodness of fit GOF, are reported in table1.

Projections of the structures for both compounds along [100] are displayed in Figure 1. The structures of $Ga_2O_3(ZnO)_9$ consist of seven tetrahedral coordination sites M01, M03, M04, M05, M06, M07 and M08, which are connected by sharing the corners of tetrahedra and build wurtzit-like partial structure, five further Trigonal-bipyramidal coordination sites M09, M10, M11, M12 and M13 connected by sharing the edges of trigonal bipyramids. Ultimately, a square-pyramid M02 is connected together with the trigonal bipyramids and the tetrahedra by sharing the corners (see figure 1 the asymmetric unit cells bellow each projected unit cells). The Trigonal bipyramids are symmetrically separated by the mirror plan $\mathbf{m_z}$ perpendicular to sliding mirror **c** and build however the similar partial structure as observed in the structure of ß-Ga_2O_3. The mirror plan passes through a

Split position which is described by M02 and M03. Instead of five trigonal-bipyramidal coordination sites as mentioned above, the compound $Ga_2O_3(ZnO)_{10}$ possess six trigonal bipyramids from M09 to M14, seven tetrahedral M01, M03, M04, M05, M06, M07 and M08 forming wurtzit-like partial structure and a square-pyramid M02. Furthermore, the polyhedra are also similarly connected as mentioned above for $Ga_2O_3(ZnO)_9$.

In the table 2 Gallium site occupancies in term of concentrations in percentage amount and corresponding cation sites with coordination numbers in parenthesis are listed. Provided that Zn occupies 100 percent both tetrahedron M01 and the square-pyramid M02 while Ga occupies 100 percent the tetrahedron M03, the iterative process of refinement has converged. To see how well Zn^{2+} and Ga^{3+}, notwithstanding their isoelectronic feature, are partitioned in the structure the data generated from the structure refinement are plotted in the figure 2. Since the site occupancy of the tetrahedra M01 and M03 and of the square pyramid M02 is set, they are moved from the plot. Given that the asymmetry unit cell generates the unit cell by the means of symmetry operations constituting the space group, we have focused our investigation on the asymmetry unit cell before extending to the unit cell. Although not perfect, the Gallium concentrations plotted against z-coordinate tend to scatter along the single trend described by the green regression line in both graphs of the figure 2. The Gallium concentrations decrease from 30 percent to zero percent and from 26 percent to zero percent for $Ga_2O_3(ZnO)_9$ and $Ga_2O_3(ZnO)_{10}$ respectively, whereas the coordination number increase with the decreasing Zinc concentration and concomitant with the increasing z-coordinate extracted from the fractional atom site coordinates (see Figures 2). Extending to unit cell the investigation reveals a modulated (Zn^{2+}, Ga^{3+}) - partition.

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	$\mathbf{Ga_2Zn_9O_{12.}}$	$\mathbf{Ga_2Zn_{10}O_{13.}}$
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)
α= ß= γ (°)	90	90
V (Å^3)	2151.31	2367.05
Z	8	8
D_x (kg.m^{-3})	5.679	5.619
$\mu_{\lambda=1.285}$ (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)	1.285	1.285
s_{max}(Å^{-1})	0.651	0.652
θ_{max}	113.6	113.95
Range of h, k, l	h = -3→2, k= -1→24, l = -42→0	h =-4→4, k =-2→24, l =-38 →0
Scan method	ω-2θ	ω-2θ
Δω	0.025	0.025
Number of measured and unique reflections	5585, 1128	2367, 1208
Refinement		
R, R_w, GOF	0.044, 0.111, 0.920	0.032, 0.086, 0.971
Number of parameters	179	171

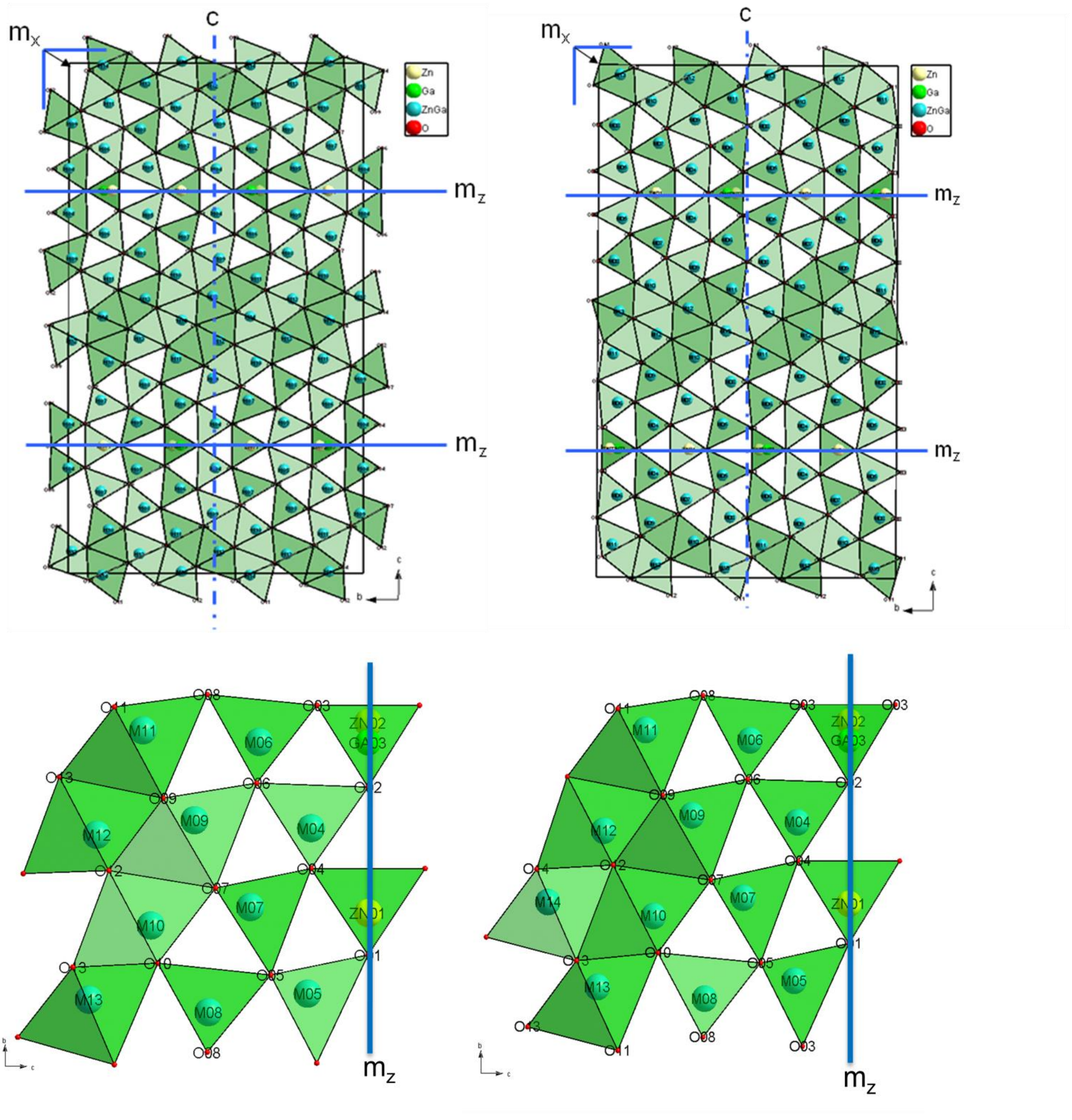

Figure 1: detailed projection of the structure model for $Ga_2O_3(ZnO)_9$ (left) and $Ga_2O_3(ZnO)_{10}$ (right) along a-axis, m_z and m_x are mirror plans and c is the sliding mirror plan. Under each projected unit cell is pictured the corresponding asymmetric unit of the structure.

Table 2: Ga-concentration (%) of both compounds derived from least square refinement.

		$Ga_2O_3(ZnO)_9$,	$Ga_2O_3(ZnO)_{10}$
Cation sites(coordination number)	Atoms	[Ga]	[Ga]
M01(4)	Ga	0	0
M02(5)	Ga	0	0
M03(4)	Ga	100	100
M04(4)	Ga	10	13
M05(4)	Ga	6	9
M06(4)	Ga	10	14
M07(4)	Ga	10	13
M08(4)	Ga	9	9
M09(5)	Ga	12	10
M10(5)	Ga	21	18
M11(5)	Ga	18	17
M12(5)	Ga	23	22
M13(5)	Ga	30	22
M14(5)			26

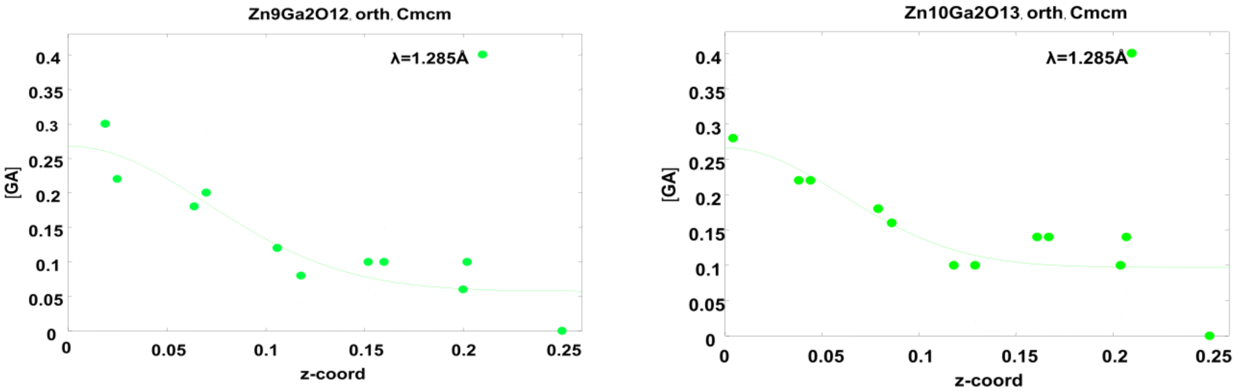

Figure 2: Ga-concentration derived from least square refinement plotted against z-coordinate extracts from the fractional atom site coordinates for both compounds. A regression analysis is graphed as a green solid line along with flow the data in the figure.

4. CONCLUDING REMARKS

For determining the Zn^{2+}- and Ga^{3+}-partition from the high resolution synchrotron radiation data the structure refinements with the reflections collected near the Zn-K-absorption edge are applied. Hence, the targeted produced scattering contrasts are exploited. 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, Rw and the goodness of fit GOF are resulted with the following values 0.044, 0.111 and 0.920 for $Ga_2O_3(ZnO)_9$ and 0.032, 0.086 and 0.971 for $Ga_2O_3(ZnO)_{10}$ respectively.

The asymmetric unit of the structure of $Ga_2O_3(ZnO)_9$ consist of seven tetrahedral coordination sites M01,M03, M04, M05, M06, M07 and M08, five Trigonal-bipyramidal coordination sites M09, M10, M11, M12 and M13 and a square-pyramidal site M02. The mirror plan contains a Split position which is described by M02 and M03. Instead of five trigonal-bipyramidal coordination sites as mentioned above the compound $Ga_2O_3(ZnO)_{10}$ possess six trigonal-bipyramidal coordination sites from M09 to M14 which display similar features as mentioned above.

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. Furthermore, this result extends to the unit cell the partition of Zn and Ga reveals a modulated variation of concentration.

Since qualitatively similar results for both compounds are found, the derived metal partitions appear as a structurally characteristic feature which, with some probability, belong to another homologous compounds of type $Ga_2O_3(ZnO)_m$ (m>8). In our next work we will extend the research on homologous compounds using the bond valence method in order to confirm and to compare the result of (Zn^{2+}, Ga^{3+}) -partitions of $Ga_2O_3(ZnO)_m$ (m=9, 10) using least square refinement.

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