

Structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$: a member of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$

Yuichi Michiue,^{a*} Noboru Kimizuka^b and Yasushi Kanke^a

^aNational Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan, and

^bYuan Ze University, 135 Yuan-tung Road, Neili, Chungli, Taoyuan 32003, Taiwan

Correspondence e-mail: michiue.yuichi@nims.go.jp

The structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ was determined using single-crystal X-ray diffraction techniques in the space group $Cmcm$. The metal ion sublattice resembles some of the Zn ions in the wurtzite ZnO structure. The oxygen ion sublattice in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ also resembles some of the O ions in ZnO. Structural relationships between $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and ZnO are discussed, illustrating the process for obtaining the centrosymmetric $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ structure from the noncentrosymmetric ZnO. Structures of phases in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are predicted on the basis of the structural data for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$. The structures of even m are constructed by simply extending the structure units seen in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$, while those of odd m consist of structure units which are of different types from those used for even m .

Received 6 February 2002

Accepted 8 July 2008

1. Introduction

Many homologous compounds based on ZnO have been reported. The most studied among them is the series $\text{In}_2\text{O}_3(\text{ZnO})_m$, which was first found in the 1960s (Kasper, 1967) and recently has drawn much attention because the compounds are candidates for photocatalysts (Kudo & Mikami, 1998), transparent conducting oxides (Moriga *et al.*, 1998) and thermoelectric materials (Ohta *et al.*, 1996). It was concluded from the lattice parameters of the phases (Kimizuka *et al.*, 1995) that the compounds have layered structures isotypic to $\text{LuFeO}_3(\text{ZnO})_m$ (Isobe *et al.*, 1994), although incommensurate modulations in In/Zn occupation were observed in $\text{In}_2\text{O}_3(\text{ZnO})_m$ (Li *et al.*, 1997). In the systems $\text{In}_2\text{O}_3\text{--}M_2\text{O}_3\text{--}ZnO$ ($M = \text{Fe, Ga, Al}$) homologous phases $\text{InMO}_3(\text{ZnO})_m$ were formed (Kimizuka *et al.*, 1989; Nakamura *et al.*, 1990, 1991, 1993). All of the $\text{InMO}_3(\text{ZnO})_m$ ($M = \text{Fe, Ga, Al}$) compounds are basically isostructural to $\text{In}_2\text{O}_3(\text{ZnO})_m$. It has been reported that the modulation character, such as the period of the occupational modulation, varies according to M (Uchida *et al.*, 1994; Li *et al.*, 1998). From a further synthetic survey in systems $M_2\text{O}_3\text{--}ZnO$ ($M = \text{Fe, Ga, Al}$), homologous series $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ were found (Kimizuka *et al.*, 1993, 1995), while no homologous phases have been reported for $M = \text{Al}$ so far. Cell parameters of orthorhombic and monoclinic forms of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ were also explained considering superstructures of $\text{In}_2\text{O}_3(\text{ZnO})_m$ (Kimizuka *et al.*, 1993). On the other hand, there is no clear relationship between the cell parameters of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ and $\text{In}_2\text{O}_3(\text{ZnO})_m$. Therefore, $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ is assumed to form a different type of structure series from those of $\text{LuFeO}_3(\text{ZnO})_m$, $\text{In}_2\text{O}_3(\text{ZnO})_m$, $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ and $\text{InMO}_3(\text{ZnO})_m$ ($M = \text{Fe, Ga, Al}$). It was suggested from an analysis using high-resolution transmission electron microscopy (Li *et al.*, 1999) that the structures of the homologous

Table 1

Crystallographic data and conditions for data collection and refinement for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$.

Crystal data	
Chemical formula	$\text{Ga}_2\text{O}_9\text{Zn}_6$
M_r	675.7
Cell setting, space group	Orthorhombic, $Cmcm$
Temperature (K)	298
a, b, c (Å)	3.2465 (9), 19.640 (5), 24.783 (6)
V (Å ³)	1580.2 (7)
Z	8
D_x (Mg m ⁻³)	5.679
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	24.63
Crystal form, color	Irregular, colorless
Crystal size (mm)	0.12 × 0.06 × 0.02
Data collection	
Diffractometer	Rigaku AFC-7R
Data collection method	ω scan
Absorption correction	φ scan
T_{\min}	0.18
T_{\max}	0.61
No. of measured, independent and observed reflections	7287, 3699, 1349
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.122
θ_{\max} (°)	45.0
No. and frequency of standard reflections	3 every 200 reflections
Intensity decay (%)	0.0
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.045, 0.101, 1.05
No. of reflections	3699
No. of parameters	113
Weighting scheme	Based on measured s.u.s; $w = 1/[\sigma^2(I) + 0.0001I^2]$
$(\Delta/\sigma)_{\max}$	0.033
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	2.32, -1.93
Extinction method	B-C type 1 Gaussian isotropic (Becker & Coppens, 1974)
Extinction coefficient	0.0078 (3)

Computer programs: JANA2000 (Petricek *et al.*, 2000).

phases $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ were noncentrosymmetric and closely related to the wurtzite structure of ZnO. In the current study the centrosymmetric structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ is clarified by a single-crystal X-ray diffraction techniques. The structural relationship between $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and ZnO is discussed, demonstrating that the centrosymmetric $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ structure can be simply derived from the noncentrosymmetric ZnO structure. Structures of other phases in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are predicted on the basis of the structural data for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$.

2. Experimental

Single crystals of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ were grown by heating a mixture of metal oxides. Ga_2O_3 and ZnO were heated separately at 1073 K for 1 d. The metal oxides in a molar ratio of $\text{Ga}_2\text{O}_3:\text{ZnO} = 1:7$ were mixed in an agate mortar for half an hour, and heated at 1923 K for 4 d in an unsealed Pt tube. The

mixture was taken out of the furnace and ground. The sample was heated again at 1923 K for 3 d in the same way.

Crystallographic data, conditions and parameters for data collection and refinement of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ are listed in Table 1.¹ Systematic reflection conditions $h + k = 2n$ for hkl and $l = 2n$ for $h0l$ lead to the possible space groups $Cmc2_1$, $C2cm$ and $Cmcm$. At the beginning, the noncentrosymmetric space group $Cmc2_1$ was chosen, and a metal ion was placed at the origin. Positions of other metal sites were determined by Fourier syntheses. Oxygen ions were successively found by Fourier syntheses and difference-Fourier syntheses. As an inversion center was seen in the structure obtained, all ions were relocated applying the space group $Cmcm$. The centrosymmetric model was confirmed, because no significant improvement in residuals was observed in the space groups $Cmc2_1$ and $C2cm$, despite the larger numbers of structural parameters. Full occupation at the metal sites was assumed except for $M7$ and $M8$. The distance between $M7$ and $M8$ is so close that it is impossible for the two sites to be occupied simultaneously by metal ions. Therefore, the sum of occupation factors at the two sites was fixed at unity. Further, $M8$ was slightly moved away from the mirror plane $z = 1/4$ so as to reduce U^{33} . It was also found that O5 should be put at a position deviating from the mirror plane $x = 0$. As the refinement of the Ga/Zn ratio at a site using X-ray diffraction data is almost impossible, bipyramidal sites ($M4$ and $M9$) were tentatively allotted to Ga and the remainder were for Zn in refinements.

3. Results and discussion

3.1. Structure description of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$

The structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ is projected along **a** (Fig. 1). Metal–oxygen distances less than 2.5 Å are listed in Table 2. The $M7$ ion on the mirror plane at $z = 1/4$ has tetrahedral coordination. (Note that the occupation factor of O5 is 0.5.) The $M3$ ion on the mirror plane is also tetrahedral. On the other hand, trigonal bipyramidal coordination is seen for $M4$ at $z = 1/2$, which is located midway between the two mirror planes at $z = 1/4$ and $z = 3/4$. Thus, the coordination number is 4 for $M3$ and $M7$, and 5 for $M4$. It is not easy to determine the coordination number of other metal ions, because the coordination number depends on the threshold of the M –O distance regarded as a bond. The coordination environment of the metal ions gradually changes according to their positions (z coordinates). It is generally seen that the closer to a mirror plane a metal ion is, the closer to four-coordination is the environment of the metal ion. For example, $M6$ near the mirror plane has four $M6$ –O distances less than 2.00 Å and one longer $M6$ –O1 [3.123 (6) Å], and $M10$ also near the mirror plane has four $M10$ –O distances less than 1.97 Å and one longer $M10$ –O6 [2.955 (6) Å]. These metal sites are considered to be tetrahedral sites, as the distance of the fifth

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: KD5022). Services for accessing these data are described at the back of the journal.

nearest $M-O$ pair is too long to be regarded as a chemical bond. On the other hand, for $M9$ far away from the mirror planes, the distance to the fifth nearest oxygen ion, $M9-O9 = 2.290$ (6) Å, is close to the other four $M9-O$ distances ranging from 1.921 to 2.030 Å, which may allow us to conclude that this metal site is five-coordinate. The gradual change of coordination environment for metal ions is also seen in structures of the homologous series $\text{LuFeO}_3(\text{ZnO})_m$ (Isobe *et al.*, 1994). The uncommon coordination environment of the metal ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ is understood by considering the derivation of the $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ structure from the ZnO structure, which will be discussed in §3.2. It should be noted that the above coordination character of metal sites in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ is not the case for $M8$, which is surrounded by five oxygen ions forming a square pyramid.

3.2. Structural relationship between $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and ZnO

In order to compare the structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ to the wurtzite structure of ZnO , the projection along \mathbf{a} of the former is drawn in Fig. 2(a) (where deviations of $M8$ and $O5$ sites from mirror planes are ignored for simplicity) and the projection along the a axis of the latter, \mathbf{a}_{ZnO} , is in Fig. 2(b). In Fig. 2(a) metal ions at the same fractional coordinate x are connected by bonds so that zigzag chains of metal ions are easily recognized. Similarly, Zn ions at the same X are connected by bonds in Fig. 2(b), where X is the fractional coordinate for an axis $\mathbf{A} = \mathbf{a}_{\text{ZnO}}$. The zigzag arrangements are also seen for oxygen ions. Clearly, the structure unit between the two mirror planes $m1$ and $m2$ in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ resembles

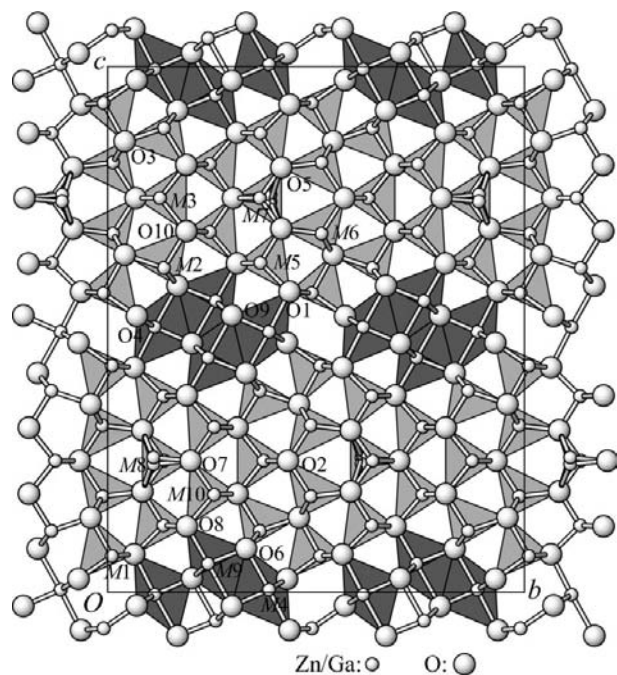


Figure 1
Structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ projected along \mathbf{a} . Interatomic distances less than 2.5 Å between metal and oxygen ions are indicated by bonds. Trigonal bipyramids are shown with darker shading and the tetrahedra are shown by lighter shading, representing the coordination between metal and oxygen ions.

Table 2
Selected interatomic distances (Å) between metal and oxygen ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$.

$M1-O1^i$	1.939 (3)	$M7-O5$	1.780 (8)
$M1-O1^{ii}$	1.939 (3)	$M7-O5^v$	1.780 (8)
$M1-O3^{iii}$	2.068 (5)	$M7-O5^{xv}$	1.780 (8)
$M1-O4^{iv}$	1.901 (7)	$M7-O5^{xi}$	1.780 (8)
		$M7-O7^{viii}$	2.051 (5)
		$M7-O7^{ix}$	2.051 (5)
$M2-O3^v$	1.951 (5)		
$M2-O6^{vi}$	1.938 (3)	$M8-O5^{viii}$	2.493 (11)
$M2-O6^{vii}$	1.938 (3)	$M8-O5^{ix}$	2.196 (12)
$M2-O10$	2.032 (5)	$M8-O5^i$	2.302 (11)
		$M8-O5^{ii}$	1.977 (11)
$M3-O2^{viii}$	1.988 (4)	$M8-O5^{xvi}$	2.196 (12)
$M3-O2^{ix}$	1.988 (4)	$M8-O5^{xvii}$	2.493 (11)
$M3-O10$	1.991 (5)	$M8-O5^{xviii}$	1.977 (11)
$M3-O10^v$	1.991 (5)	$M8-O5^{xix}$	2.302 (11)
		$M8-O7$	1.761 (9)
$M4-O1^x$	2.131 (6)		
$M4-O4^i$	1.901 (4)	$M9-O6$	1.930 (6)
$M4-O4^{ii}$	1.901 (4)	$M9-O8$	2.030 (6)
$M4-O6$	2.226 (6)	$M9-O9^x$	2.290 (6)
$M4-O9^x$	1.915 (5)	$M9-O9^i$	1.921 (3)
		$M9-O9^{ii}$	1.921 (3)
$M5-O1$	1.930 (6)		
$M5-O5^v$	1.898 (8)	$M10-O7$	1.942 (5)
$M5-O5^{xi}$	1.898 (8)	$M10-O8$	1.964 (6)
$M5-O8^{vi}$	1.968 (3)	$M10-O10^i$	1.961 (3)
$M5-O8^{vii}$	1.968 (3)	$M10-O10^{ii}$	1.961 (3)
$M6-O2^{xii}$	1.985 (4)		
$M6-O3^{xiii}$	1.984 (3)		
$M6-O3^{xiv}$	1.984 (3)		
$M6-O5^v$	1.916 (8)		
$M6-O5^{xi}$	1.916 (8)		

Symmetry codes: (i) $-x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x, -y, -z + 1$; (iv) $-x, -y, z - \frac{1}{2}$; (v) $x, y, -z + \frac{3}{2}$; (vi) $-x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (viii) $-x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (ix) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (x) $x, y, -z + \frac{1}{2}$; (xi) $-x, y, -z + \frac{3}{2}$; (xii) $-x, -y + 1, -z + 1$; (xiii) $x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (xiv) $x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (xv) $-x, y, z$; (xvi) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (xvii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (xviii) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (xix) $x + \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$.

the structure of ZnO , as suggested by high-resolution lattice imaging in transmission electron microscopy (Li *et al.*, 1999). However, two primary differences are found between the two structures. First, $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ has an inversion center as indicated by i in Fig. 2(a), while ZnO has a noncentrosymmetric structure (space group $P6_3mc$). Second, the distance between the neighboring metal ions in the zigzag chain is longer than that between neighboring oxygen ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$, while the two distances are equal in ZnO . That is, the density of metal ions is lower than that of oxygen ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$, which coincides with the fact that the number of metal ions, eight, is smaller than that of oxygen ions, nine, in the chemical formula.

Considering metal and oxygen ions separately, it is recognized that the structure of metal ions in a block between $m1$ and $m2$ in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ (Fig. 2a) resembles the structure of Zn ions in a block between the two planes CZO6 and CZ6 shown in Fig. 2(b), while the structure of O ions in a block between $m1$ and $m2$ in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ (Fig. 2a) resembles the structure of O ions in a block between the two planes CZO6 and CO6 shown in Fig. 2(b). The distance between $m1$ and $m2$ (12.393 Å) is a little longer than that between CZO6 and CZ6 , but shorter than that between CZO6 and CO6 . When only Zn

ions are considered in the ZnO structure, an inversion center is found as indicated by i_{Zn} in Fig. 2(b). Similarly, when only

oxygen ions are considered, an inversion center i_O is found, which deviates a little from i_{Zn} . The structure unit between $m1$ and $m2$ in $Ga_2O_3(ZnO)_6$ is given by modification of the ZnO structure in three steps. As the first step, the structure unit of only Zn ions defined by six planes $X = 0, X = 1, B1Z, B2Z, CZO6, CZ6$ (Fig. 2b) was taken from the ZnO structure. This Zn unit (Fig. 2c) has an inversion center i_{Zn} . Planes B1Z and B2Z are normal to the vector $\mathbf{B} = 3\mathbf{a}_{ZnO} + 6\mathbf{b}_{ZnO} + 2\mathbf{c}_{ZnO}$, and the distance between B1Z and B2Z is equal to $|\mathbf{B}|$. Planes CZO6 and CZ6 are parallel to \mathbf{A} and \mathbf{B} , and the distance between CZO6 and CZ6 is $2(\mathbf{C} \cdot \mathbf{C}_p)$, where $\mathbf{C} = -\mathbf{a}_{ZnO}/2 - \mathbf{b}_{ZnO} + \mathbf{c}_{ZnO}$ and \mathbf{C}_p is a unit vector ($|\mathbf{C}_p| = 1$) normal to \mathbf{A} and \mathbf{B} . Similarly, a structure unit of only O ions defined by six planes $X = 0, X = 1, B1O, B2O, CZO6$ and $CO6$ (Fig. 2b) was taken from the ZnO structure. This O unit (Fig. 2d) also has an inversion center i_O . Planes B1O and B2O are normal to \mathbf{B} , and the distance between B1O and B2O is equal to $|\mathbf{B}|$. The CO6 plane is parallel to \mathbf{A} and \mathbf{B} , and the distance between CZO6 and CO6 is $9(\mathbf{C} \cdot \mathbf{C}_p)/4$. In the second step, the Zn unit is expanded along \mathbf{C}_p (Fig. 2e), so that the distance between CZO6 and CZ6 is equal to the distance between $m1$ and $m2$ in the $Ga_2O_3(ZnO)_6$ structure, 12.393 Å. On the other hand, the O unit is contracted along \mathbf{C}_p (Fig. 2f), so that the distance between CZO6 and CO6 is also equal to the distance between $m1$ and $m2$. In the third step the two structure units are superposed so that inversion centers of the two units, i_{Zn} and i_O , coincide with each other. The derived structure unit (Fig. 2g), which has an inversion center as a whole, is basically equal to the structure unit between $m1$ and $m2$ in $Ga_2O_3(ZnO)_6$ (Fig. 2a) considering the partial substitution of Ga for Zn. It is noted that $M7$ is not included in the structure model derived by the above process. Instead, $M8$ is fully occupied. Therefore, part of the metal ions at the $M8$ site should be moved to the $M7$ site in order to obtain the real structure of $Ga_2O_3(ZnO)_6$.

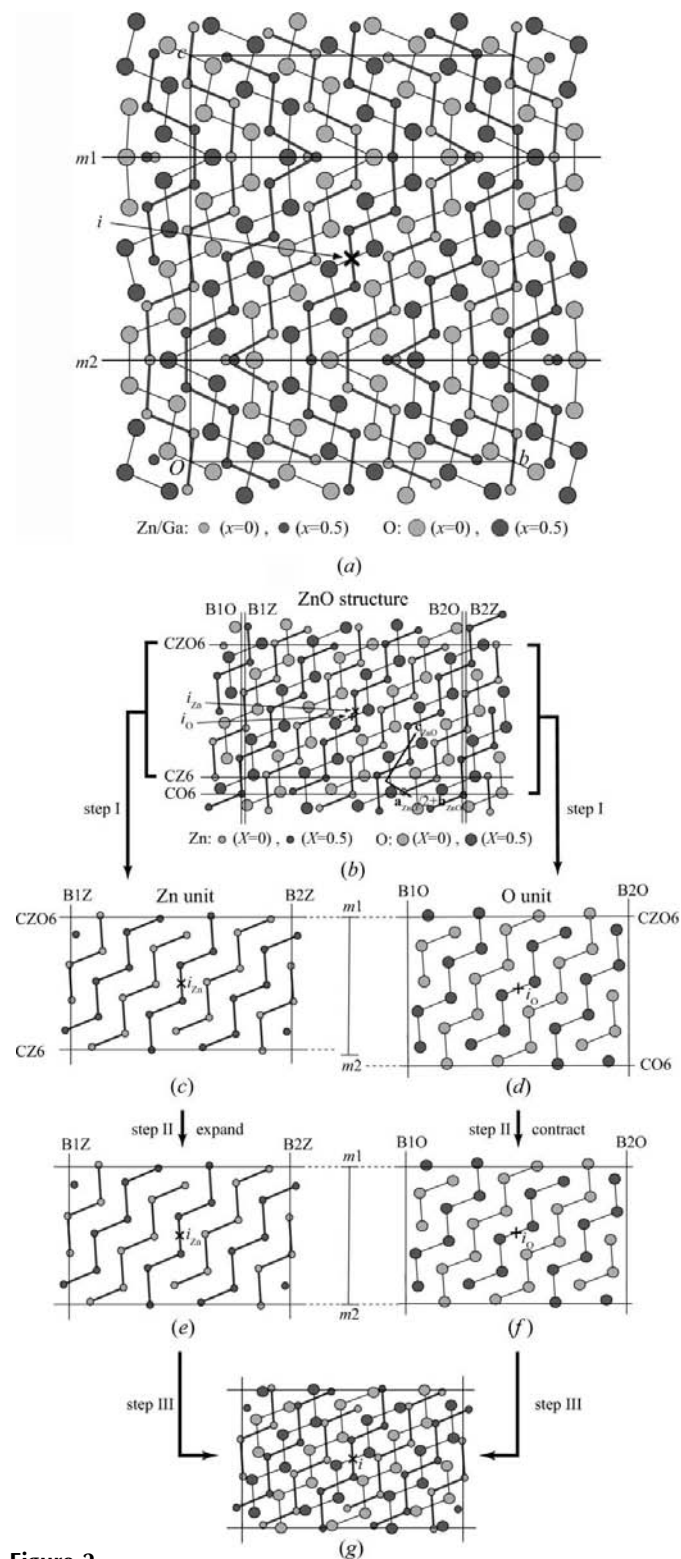


Figure 2 Comparison of structures $Ga_2O_3(ZnO)_6$ and wurtzite ZnO. (a) $Ga_2O_3(ZnO)_6$ structure, (b) ZnO structure projected along \mathbf{a}_{ZnO} , (c) Zn unit extracted from the ZnO structure, (d) O unit extracted from the ZnO structure, (e) expanded Zn unit, (f) contracted O unit, and (g) superposition of (e) and (f).

3.3. Prediction of structures in the homologous series $Ga_2O_3(ZnO)_m$

All the phases in the homologous series $Ga_2O_3(ZnO)_m$ have roughly the same unit-cell dimensions a and b , while the dimension c varies according to the composition parameter m ; $c = 27.745$ (4), 30.684 (3) and 33.603 (5) Å for $m = 7, 8$ and 9, respectively (Kimizuka *et al.*, 1995). Considering these facts, it is assumed that structures of m larger than 6 are constructed by extending the structure unit in $Ga_2O_3(ZnO)_6$ along \mathbf{c} . The structure models for the phases can be obtained from the ZnO structure in a similar manner to that used for the derivation of the $Ga_2O_3(ZnO)_6$ structure.

The Zn unit defined by planes $X = 0, X = 1, B1Z, B2Z, CZO6, CZ6$ was taken for construction of the $Ga_2O_3(ZnO)_6$ structure, while another Zn unit defined by planes $X = 0, X = 1, B1Z, B2Z, CZO8, CZ8$ in Fig. 3(a) can be taken in order to make up the $Ga_2O_3(ZnO)_8$ structure. (It is noted that CZ8 is equal to CO6.) The distance between CZO8 and CZ8 is $5(\mathbf{C} \cdot \mathbf{C}_p)/2$. This extended unit of Zn ions has an inversion center i_{Zn} , which coincides with the inversion center of the Zn unit used for the $Ga_2O_3(ZnO)_6$ structure. As for the oxygen

ions, the structure unit defined by the planes $X = 0, X = 1, B1O, B2O, CZO6, CO6$ for the $Ga_2O_3(ZnO)_6$ structure should be replaced by an extended unit defined by planes $X = 0, X = 1, B1O, B2O, CZO8, CO8$ for the $Ga_2O_3(ZnO)_8$ structure (Fig. 3a). The distance between CZO8 and CO8 is $11(\mathbf{C} \cdot \mathbf{C}_p)/4$. This extended unit of O ions has an inversion center i_O , which coincides with the inversion center of the O unit for the $Ga_2O_3(ZnO)_6$ structure. As done in the process for constructing the $Ga_2O_3(ZnO)_6$ structure, the Zn unit is expanded and the O unit is contracted along \mathbf{C}_p , so that distances between CZO8 and CZ8, and between CZO8 and CO8 both become 15.342 \AA , which is a half c in $Ga_2O_3(ZnO)_8$. Then the two units are superposed so that inversion centers of

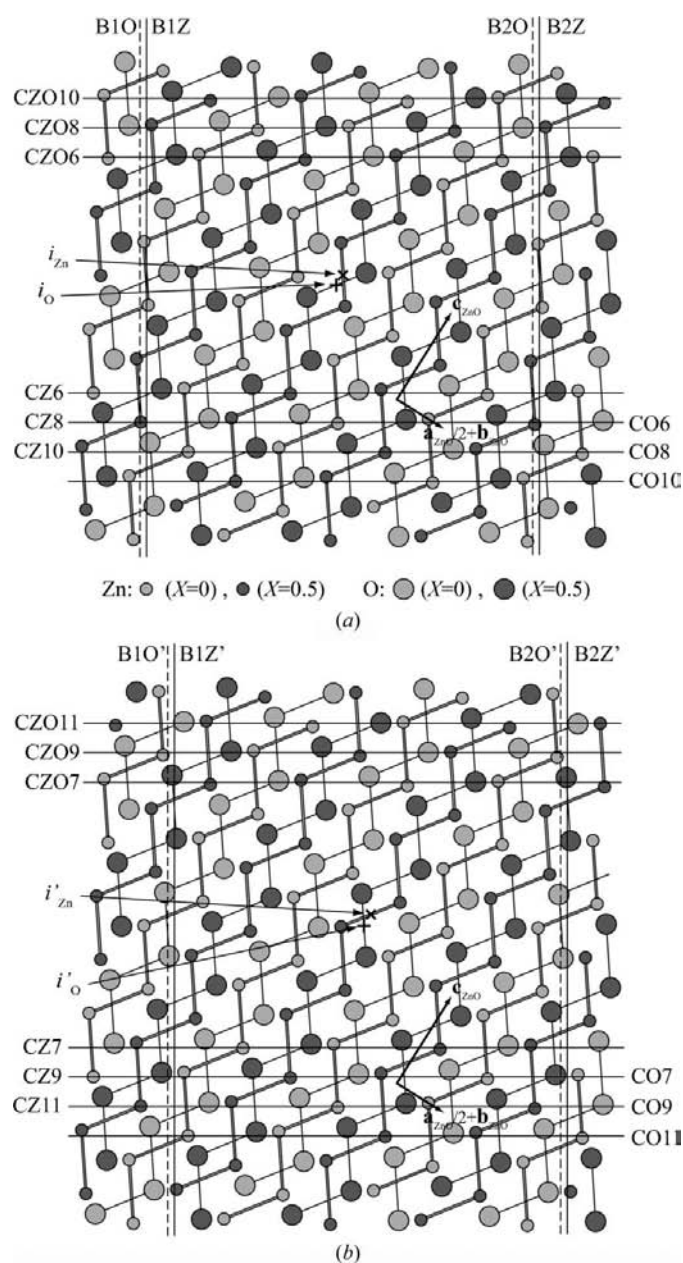


Figure 3
Definition of structure units for derivation of $Ga_2O_3(ZnO)_m$ with (a) even and (b) odd m .

the two structures, i_{Zn} and i_O , coincide with each other. The obtained structure unit with an inversion center can be substituted for the unit between $m1$ and $m2$ in Fig. 2(a), giving the $Ga_2O_3(ZnO)_8$ structure. In general, structure models for phases of even m larger than 6 are given by the same process to the one above using planes $CZOm, CZm$ and COm in Fig. 3(a). The distance between $CZOm$ and CZm is $(m + 2)(\mathbf{C} \cdot \mathbf{C}_p)/4$, and the distance between $CZOm$ and COm is $(m + 3)(\mathbf{C} \cdot \mathbf{C}_p)/4$. Obviously, structures of phases for even m smaller than 6 can also be derived by narrowing the range of the units, although the formation of such phases has not yet been reported.

Prediction of structures for odd m is not as straightforward as that for even m . However, it is not difficult if we notice other types of inversion centers for Zn and O ions in the ZnO structure, which are indicated by i'_{Zn} and i'_O in Fig. 3(b). A new series of Zn units with an inversion center i'_{Zn} are defined by the planes $X = 0, X = 1, B1Z', B2Z', CZOm, CZm$ as shown in Fig. 3(b). A new series of O units with an inversion center i'_O are also defined by the planes $X = 0, X = 1, B1O', B2O', CZOm, COm$. The distance between $CZOm$ and CZm is $(m + 2)(\mathbf{C} \cdot \mathbf{C}_p)/4$, and the distance between $CZOm$ and COm is $(m + 3)(\mathbf{C} \cdot \mathbf{C}_p)/4$ for odd m as well as even m . The length $c/2$ of $Ga_2O_3(ZnO)_m$ ($m = 7, 9, \dots$) is a little longer than the distance between $CZOm$ and CZm , but a little shorter than that between $CZOm$ and COm . The two types of structure units are taken for constructing the $Ga_2O_3(ZnO)_m$ structures of odd m in the same manner as that used for even m .

Considering the process of deriving the structures in the homologous series $Ga_2O_3(ZnO)_m$ from the wurtzite structure of ZnO, it is obvious that the structures of the series can be treated as commensurate phases of the compositely modulated structures, where the basic period along \mathbf{c} for the Zn ions is different from that for O ions. The unified description applying the superspace formalism for the structures is in progress.

References

- Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147.
 Isobe, M., Kimizuka, N., Nakamura, M. & Mohri, T. (1994). *Acta Cryst.* **C50**, 332–336.
 Kasper, H. (1967). *Z. Anorg. Allg. Chem.* **349**, 113–123.
 Kimizuka, N., Isobe, M. & Nakamura, M. (1995). *J. Solid State Chem.* **116**, 170–178.
 Kimizuka, N., Isobe, M., Nakamura, M. & Mohri, T. (1993). *J. Solid State Chem.* **103**, 394–402.
 Kimizuka, N., Mohri, T. & Nakamura, M. (1989). *J. Solid State Chem.* **81**, 70–77.
 Kudo, A. & Mikami, I. (1998). *Chem. Lett.* pp. 1027–1028.
 Li, C. F., Bando, Y., Nakamura, M. & Kimizuka, N. (1997). *J. Electron Microsc.* **46**, 119–127.
 Li, C. F., Bando, Y., Nakamura, M., Onoda, M. & Kimizuka, N. (1998). *J. Solid State Chem.* **139**, 347–355.
 Li, C., Bando, Y., Nakamura, M., Kurashima, K. & Kimizuka, N. (1999). *Acta Cryst.* **B55**, 355–362.
 Moriga, T., Edwards, D. D., Mason, T. O., Palmer, G. B., Poepelmeier, K. R., Schindler, J. L., Kannewurf, C. R. & Nakabayashi, I. (1998). *J. Am. Ceram. Soc.* **81**, 1310–1316.

- Nakamura, M., Kimizuka, N. & Mohri, T. (1990). *J. Solid State Chem.* **86**, 16–40.
- Nakamura, M., Kimizuka, N. & Mohri, T. (1991). *J. Solid State Chem.* **93**, 298–315.
- Nakamura, M., Kimizuka, N., Mohri, T. & Isobe, M. (1993). *J. Solid State Chem.* **105**, 535–549.
- Ohta, H., Seo, W. S. & Koumoto, K. (1996). *J. Am. Ceram. Soc.* **79**, 2193–2196.
- Petricek, V., Dusek, M. & Palatinus, L. (2000). *JANA2000*. Institute of Physics, Prague, Czech Republic.
- Uchida, N., Bando, Y., Nakamura, M. & Kimizuka, N. (1994). *J. Electron Microsc.* **43**, 146–150.