

Structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ and a unified description of the homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$

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The structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ has been determined by a single-crystal X-ray diffraction technique. In the monoclinic structure of the space group $C2/m$ with cell parameters $a = 19.66(4)$, $b = 3.2487(5)$, $c = 27.31(2)$ Å, and $\beta = 105.9(1)^\circ$, a unit cell is constructed by combining the halves of the unit cell of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_7$ in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$. The homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ is derived and a unified description for structures in the series is presented using the $(3+1)$ -dimensional superspace formalism. The phases are treated as compositely modulated structures consisting of two subsystems. One is constructed by metal ions and another is by O ions. In the $(3+1)$ -dimensional model, displacive modulations of ions are described by the asymmetric zigzag function with large amplitudes, which was replaced by a combination of the sawtooth function in refinements. Similarities and differences between the two homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are clarified in $(3+1)$ -dimensional superspace. The validity of the $(3+1)$ -dimensional model is confirmed by the refinements of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$, while a few complex phenomena in the real structure are taken into account by modifying the model.

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1. Introduction

ZnO of the wurtzite structure is one of the most useful ceramics. Electrical conductivity is generally enhanced for ZnO doped with trivalent metal ions, such as Al, Ga *etc.* Only a slight amount of the trivalent metal ions can replace the divalent Zn ion retaining the wurtzite structure. When the amount of doping ions exceeds the solubility limit a series of compounds with long-period structures, that is the homologous series, are formed instead of the wurtzite structure. Extensive studies have been performed for the homologous phases $\text{In}_2\text{O}_3(\text{ZnO})_m$ (Kasper, 1967) and related compounds, because the materials are candidates for photocatalysts (Kudo & Mikami, 1998), transparent conducting oxides (Moriga *et al.*, 1998) and thermoelectric materials (Ohta *et al.*, 1996). Phases in $\text{In}_2\text{O}_3(\text{ZnO})_m$ are isotypic to $\text{LuFeO}_3(\text{ZnO})_m$ (Isobe *et al.*, 1994). Structures of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ are also understood as superstructures of $\text{In}_2\text{O}_3(\text{ZnO})_m$ (Kimizuka *et al.*, 1993). Furthermore, homologous phases $\text{InMO}_3(\text{ZnO})_m$ are found in systems $\text{In}_2\text{O}_3\text{--}M_2\text{O}_3\text{--}ZnO$ ($M = \text{Fe, Ga, Al}$; Kimizuka *et al.*, 1989; Nakamura *et al.*, 1990, 1991, 1993), which are basically isotypic to $\text{In}_2\text{O}_3(\text{ZnO})_m$. On the other hand, the structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Kimizuka *et al.*, 1995), which was first examined by high-resolution transmission electron microscopy (Li *et al.*, 1999) and recently determined by single-crystal X-ray diffraction (Michiue *et al.*, 2008; Michiue & Kimizuka, 2010), is fundamentally different from the $\text{In}_2\text{O}_3(\text{ZnO})_m$ type. First-

Table 1Crystallographic data and conditions for data collection and refinement for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$.

Crystal data	
Chemical formula	$\text{Ga}_4\text{Zn}_{13}\text{O}_{19}$
M_r	1432.8
Crystal system, space group	Monoclinic, $C2/m$
a, b, c (Å)	19.66 (4), 3.2487 (5), 27.31 (2)
β	105.9 (1)
V (Å ³)	1678 (4)
Z	4
D_x (Mg m ⁻³)	5.671
Radiation	Mo $K\alpha$
μ (mm ⁻¹)	24.61
Crystal size (mm)	0.12 × 0.10 × 0.02
Data collection	
Diffractometer	Four-circle
Scan method	ω scans
Absorption correction	φ scans
T_{\min}, T_{\max}	0.466, 0.996
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14 188, 7763, 4676
R_{int}	0.088
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	1.002
θ_{max} (°)	45.39
Range of h, k, l	$h = 0 \rightarrow 38, k = -6 \rightarrow 6, l = -54 \rightarrow 52$
No. and frequency of standard reflections	Every 150 reflections
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.061, 0.195, 2.88
No. of reflections	7763
No. of parameters	225
No. of restraints	0
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	-3.59, -3.74
Extinction method	B-C type 1 Gaussian isotropic (Becker & Coppens, 1974)
Extinction coefficient	310 (20)

principle calculations were carried out for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ (Da Silva *et al.*, 2009). Recently, the material was found to be a new transparent conducting oxide and also to have promising thermoelectric properties (Michiue *et al.*, 2011).

A unified description for structures in the series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ was presented using the (3 + 1)-dimensional superspace description (Michiue & Kimizuka, 2010), in which the structures were treated as commensurate phases of the compositely modulated structures (Yamamoto, 1996; van Smaalen, 1995). The superspace formalism was originally developed for the analysis of incommensurate structures (de Wolff, 1974; Janner & Janssen, 1980*a,b*), and later proved to be efficient for the description of commensurate phases (van Smaalen, 1987; Yamamoto *et al.*, 1985; Perez-Mato *et al.*, 1987). Furthermore, the introduction of discontinuous modulation functions such as the crenel function and the sawtooth function has enabled the unified description of long-period structures such as layered perovskites of Arivillius phases (Boullay *et al.*, 2002) and Ruddlesden–Popper phases (Elcoro *et al.*, 2001, 2004), hexagonal perovskites (Evain *et al.*, 1998; Perez-Mato *et al.*, 1999), metal-deficient perovskites (Elcoro *et al.*, 2000; Boullay *et al.*, 2003), shear structures (Michiue *et al.*, 2005, 2006, 2007), and hexagonal ferrites (Orlov *et al.*, 2007). In the (3 + 1)-dimensional description for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$

displacive modulations of ions in the structures were defined by the zigzag function with large amplitudes. This originated from the unique character of the structures in the series, namely construction by a kind of unit-cell twinning as classified by Hyde *et al.* (1979). Similar features are observed in minerals with modular structures (Elcoro *et al.*, 2008).

In this study a single crystal of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ was found and the structure was determined by X-ray diffraction. A unit cell of the structure is basically constructed by combining halves of the unit cell of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_7$ in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue *et al.*, 2008). Consequently, a homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ is derived, and a unified description of structures in the series was presented using the (3 + 1)-dimensional superspace description. Similarities and differences between the two homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ were discussed. It is noted that similar variations are reported in minerals with modular structures. In the lillianite homologous series, for example, individual structures are described by the symbol $^{N_1, N_2}L$ where N_1 and N_2 describe the width of adjacent modules (Makovicky & Karop-Møller, 1977). The sizes of two adjacent modules can be different in general, although the unified description is given for $^{N, N}L$ members with the same size for all modules (Elcoro *et al.*, 2008).

In the following section the experimental details are discussed. In §3 the structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ is described by the conventional method in three-dimensional space, and a homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ is derived. In §4 a unified description of structures in the homologous phases $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ is presented. In the first part an idealized structure model is defined in three-dimensional space. In part 2 the model is treated as a compositely modulated structure and translated into a (3 + 1)-dimensional model. It is shown that there are some possible ways for the setting of subsystems. In the last part the validity of the model is confirmed by refinements of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$. The (3 + 1)-dimensional model is modified to deal with a few complex phenomena in real structures.

2. Experimental

A single crystal of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ was obtained from the product in our previous study for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ (Michiue *et al.*, 2008). 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 30 min, 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 1023 K for 3 d in the same way. Intensity data were collected for a single-crystal mounted on a point-detector diffractometer (Rigaku AFC 7R).

Crystallographic data, conditions and parameters for data collection and refinement of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ are listed in Table 1. The positions of most metal ions for an initial structure model were deduced from structures of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_7$ in our previous study (Michiue *et al.*, 2008). Other ions were located in Fourier syntheses and difference-

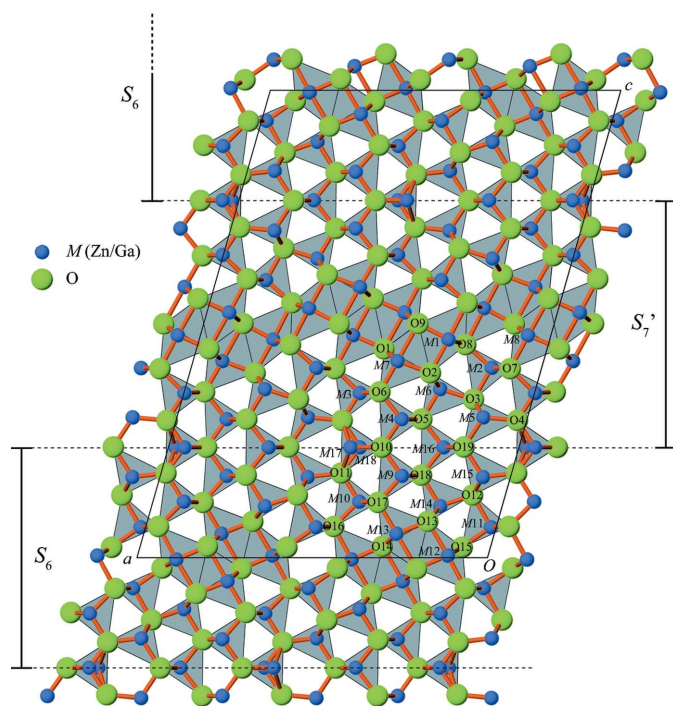


Figure 1
Structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ projected along **b**.

Fourier syntheses. Atomic parameters are given in the supplementary material.¹ Full occupations at the metal sites were assumed except for *M17* and *M18*. As the distance between *M17* and *M18* is too close to be simultaneously occupied, the sum of occupation factors at the two sites was fixed to unity. The occupation ratio was *M17*:*M18* = 0.46:0.54. Despite the large U_{22} for *M17*, *O4*, *O10* and *O11*, all of these ions were put on the mirror plane $y = 0$, because the U_{22} values were reduced little even when these ions were moved off the mirror plane. No vacancy for O ions was assumed and the Ga:Zn ratio 4:13 was deduced from the charge neutrality for a whole structure in a unit cell. As the determination of the Ga/Zn ratio at each site using X-ray diffraction data is almost impossible, the Ga/Zn ratio was fixed at 4/13, or 4/(2*n* + 1) in general for all metal sites. Programs used: *JANA2006* (Petricek *et al.*, 2006) for calculations, and *VESTA* (Momma & Izumi, 2008) and *ATOMS* (Dowty, 2005) for graphics.

3. Structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$

Projection of the structure for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ along **b** is given in Fig. 1. *M*–*O* distances less than 2.5 Å are listed in Table 2. Coordination numbers of the metal sites are 4 or 5, which change according to the limit of the *M*–*O* distance included as a coordination. Partially occupied metal positions *M17* and *M18* are found. *M17* is a square-pyramidal coordination site, while *M18* is a tetrahedral site. These features are

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: DK5003). Services for accessing these data are described at the back of the journal.

Table 2
Selected interatomic distances (Å) in $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$.

<i>M1</i> – <i>O2</i>	2.143 (8)	<i>M10</i> – <i>O11</i>	1.889 (9)
<i>M1</i> – <i>O8</i>	2.297 (9)	<i>M10</i> – <i>O16</i> ⁱⁱⁱ	1.986 (9)
<i>M1</i> – <i>O8</i> ⁱ	1.911 (4)	<i>M10</i> – <i>O17</i> ^{iv}	1.952 (5)
<i>M1</i> – <i>O8</i> ⁱⁱ	1.911 (4)	<i>M10</i> – <i>O17</i> ^v	1.952 (5)
<i>M1</i> – <i>O9</i> ⁱⁱⁱ	1.911 (11)	<i>M11</i> – <i>O12</i>	2.062 (9)
<i>M2</i> – <i>O3</i>	2.037 (8)	<i>M11</i> – <i>O15</i> ⁱⁱⁱ	1.970 (14)
<i>M2</i> – <i>O7</i> ^{iv}	1.939 (4)	<i>M11</i> – <i>O16</i> ^{iv}	1.921 (5)
<i>M2</i> – <i>O7</i> ^v	1.939 (4)	<i>M11</i> – <i>O16</i> ^v	1.921 (5)
<i>M2</i> – <i>O8</i> ⁱⁱⁱ	1.940 (10)	<i>M12</i> – <i>O13</i>	2.221 (11)
<i>M3</i> – <i>O4</i>	1.829 (11)	<i>M12</i> – <i>O14</i> ^{vi}	1.897 (12)
<i>M3</i> – <i>O6</i> ^{iv}	1.979 (5)	<i>M12</i> – <i>O15</i> ⁱ	1.870 (7)
<i>M3</i> – <i>O6</i> ^v	1.979 (5)	<i>M12</i> – <i>O15</i> ⁱⁱ	1.870 (7)
<i>M3</i> – <i>O7</i> ⁱⁱⁱ	1.936 (9)	<i>M12</i> – <i>O16</i> ^{vii}	2.106 (9)
<i>M4</i> – <i>O5</i> ⁱ	1.981 (5)	<i>M13</i> – <i>O13</i> ⁱⁱⁱ	1.881 (11)
<i>M4</i> – <i>O5</i> ⁱⁱ	1.981 (5)	<i>M13</i> – <i>O14</i> ^{viii}	2.270 (11)
<i>M4</i> – <i>O6</i> ⁱⁱⁱ	1.967 (9)	<i>M13</i> – <i>O14</i> ^{iv}	1.937 (6)
<i>M4</i> – <i>O10</i>	1.924 (9)	<i>M13</i> – <i>O14</i> ^v	1.937 (6)
<i>M5</i> – <i>O3</i> ^{iv}	1.990 (4)	<i>M13</i> – <i>O17</i>	2.034 (9)
<i>M5</i> – <i>O3</i> ^v	1.990 (4)	<i>M14</i> – <i>O12</i> ⁱⁱⁱ	1.914 (10)
<i>M5</i> – <i>O4</i> ⁱⁱⁱ	1.926 (12)	<i>M14</i> – <i>O13</i> ⁱ	1.970 (6)
<i>M5</i> – <i>O19</i>	1.998 (8)	<i>M14</i> – <i>O13</i> ⁱⁱ	1.970 (6)
<i>M6</i> – <i>O2</i> ⁱ	1.947 (4)	<i>M14</i> – <i>O18</i>	2.019 (8)
<i>M6</i> – <i>O2</i> ⁱⁱ	1.947 (4)	<i>M15</i> – <i>O11</i> ⁱⁱⁱ	1.890 (11)
<i>M6</i> – <i>O3</i> ⁱⁱⁱ	1.954 (11)	<i>M15</i> – <i>O12</i> ^{iv}	2.008 (5)
<i>M6</i> – <i>O5</i>	1.979 (7)	<i>M15</i> – <i>O12</i> ^v	2.008 (5)
<i>M7</i> – <i>O1</i> ^{iv}	1.917 (4)	<i>M15</i> – <i>O19</i>	1.985 (8)
<i>M7</i> – <i>O1</i> ^v	1.917 (4)	<i>M16</i> – <i>O5</i> ⁱⁱⁱ	1.995 (9)
<i>M7</i> – <i>O2</i> ⁱⁱⁱ	1.947 (11)	<i>M16</i> – <i>O18</i> ⁱⁱⁱ	2.005 (8)
<i>M7</i> – <i>O6</i>	2.012 (8)	<i>M16</i> – <i>O19</i> ^{iv}	1.986 (5)
<i>M7</i> – <i>O9</i>	2.393 (10)	<i>M16</i> – <i>O19</i> ^v	1.986 (5)
<i>M8</i> – <i>O1</i>	2.344 (10)	<i>M17</i> – <i>O4</i> ^{iv}	2.268 (7)
<i>M8</i> – <i>O1</i> ⁱⁱⁱ	1.904 (11)	<i>M17</i> – <i>O4</i> ^v	2.268 (7)
<i>M8</i> – <i>O7</i>	2.131 (8)	<i>M17</i> – <i>O10</i> ⁱⁱⁱ	1.753 (11)
<i>M8</i> – <i>O9</i> ^{iv}	1.907 (4)	<i>M17</i> – <i>O11</i> ^{iv}	2.238 (7)
<i>M8</i> – <i>O9</i> ^v	1.907 (4)	<i>M17</i> – <i>O11</i> ^v	2.238 (7)
<i>M9</i> – <i>O10</i>	1.962 (9)	<i>M18</i> – <i>O4</i> ^v	1.802 (10)
<i>M9</i> – <i>O17</i> ⁱⁱⁱ	1.994 (8)	<i>M18</i> – <i>O10</i> ⁱⁱⁱ	2.047 (6)
<i>M9</i> – <i>O18</i> ⁱ	1.962 (4)	<i>M18</i> – <i>O10</i> ^{ix}	2.047 (6)
<i>M9</i> – <i>O18</i> ⁱⁱ	1.962 (4)	<i>M18</i> – <i>O11</i> ^v	1.776 (10)

Symmetry codes: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + 1$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (iii) $-x + 1, y, -z + 1$; (iv) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + 1$; (v) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + 1$; (vi) $-x + 1, y, -z + 2$; (vii) $x, y, z + 1$; (viii) $x, y, z - 1$; (ix) $-x + 1, y + 1, -z + 1$.

similar to those seen for metal sites on the mirror plane in $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ structures (Michiue *et al.*, 2008). All four-coordination sites are in a tetrahedral coordination, and connected by sharing the corners of the tetrahedra. Trigonal-bipyramidal coordination is formed at five-coordination sites except for *M18*. Neighbouring trigonal bipyramids share an edge, while a corner is shared in the connection between a tetrahedron and a trigonal bipyramid.

Tetrahedral coordination is common for Zn and Ga ions as seen in structures of ZnO and $\beta\text{-Ga}_2\text{O}_3$. The five-coordination is atypical but possible for a Zn ion. Both the trigonal bipyramid (Isobe *et al.*, 1994) and the square pyramid (Abrahams, 1967) are reported for the coordination environment of a Zn ion. The trigonal bipyramidal coordination of a Ga ion is also known (Shannon & Prewitt, 1968). No example of the square pyramidal coordination is reported for a Ga ion as far as we know, except for the compounds in $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ ($m = 6, 9$; Michiue *et al.*, 2008; Michiue & Kimizuka, 2010) and $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$. The bond-valence sum (BVS; Brown, 1996) was calculated for each metal site (Table 3). When the sites are assumed to be occupied by the Zn ion, BVSs are roughly close

Table 3
Bond-valence sum for metal sites.

	$M = \text{Zn}$	$M = \text{Ga}$
M1	2.22	2.38
M2	1.99	2.14
M3	2.20	2.36
M4	1.99	2.14
M5	1.92	2.06
M6	2.02	2.17
M7	2.23	2.40
M8	2.23	2.39
M9	1.95	2.09
M10	2.09	2.25
M11	1.98	2.12
M12	2.46	2.64
M13	2.31	2.48
M14	1.97	2.11
M15	1.95	2.09
M16	1.83	1.97
M17	1.78	1.91
M18	2.38	2.55

to the formal charge, 2. The deviation of BVS from the formal charge exceeds 0.2 for trigonal bipyramidal sites, M1, M7, M8, M12 and M13. The value is also high for the M17 site of the tetrahedral coordination. Therefore, it is expected that Ga ions have a tendency to concentrate at these sites with high BVSs.

The structural feature of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ is well understood in connection with those of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_7$, which are members of the homologous series

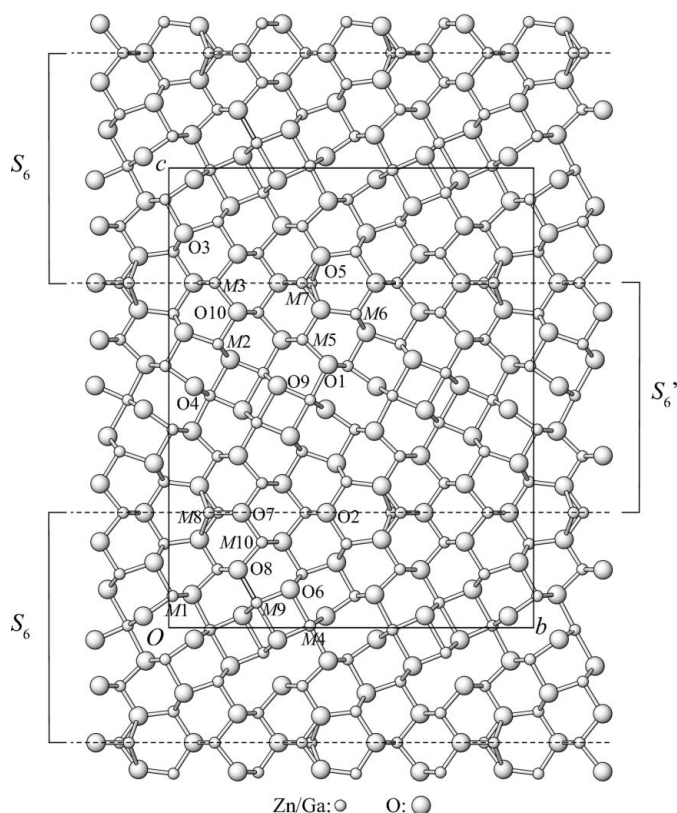


Figure 2
Structure units separated by mirror planes in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$.

$\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue *et al.*, 2008). In $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ a structure unit separated by mirror planes normal to c is seen (Fig. 2), which is expressed as an S_6 slab hereafter. [a and b in Fig. 2 are interchanged from the setting in $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$.] A structure unit related to an S_6 slab by the mirror plane is also contained in the structure, that is S_6' . The whole structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ is described as the alternate stacking of S_6 and S_6' slabs. Similarly, the structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_7$ is the alternate stacking of S_7 and S_7' slabs. Thus, structures of the homologous phases $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are considered as those constructed by the unit-cell twinning (Hyde *et al.*, 1979). A structure unit isotypic to S_6 is found in the structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$, while the remaining part is isotypic to S_7' , as indicated in Fig. 1. That is, the structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ is described as the alternate stacking of S_6 and S_7' slabs (or S_6' and S_7 slabs).

An alternate stacking of S_7 and S_8' slabs results in a new structure (Fig. 3) with the chemical composition $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{15}$ and a space group $C2/m$. Thus, a homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ is presented by a combination of S_n and S_{n+1}' slabs. As the thickness of S_n and S_{n+1}' slabs are different, the boundary of the two slabs is not a mirror plane, resulting in monoclinic symmetry for the whole structure. On the other hand, structures belonging to the $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ homologous series have orthorhombic symmetry $Cmcm$. In the following section, a unified description for structures of the homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ is discussed utilizing the $(3+1)$ -dimensional superspace description.

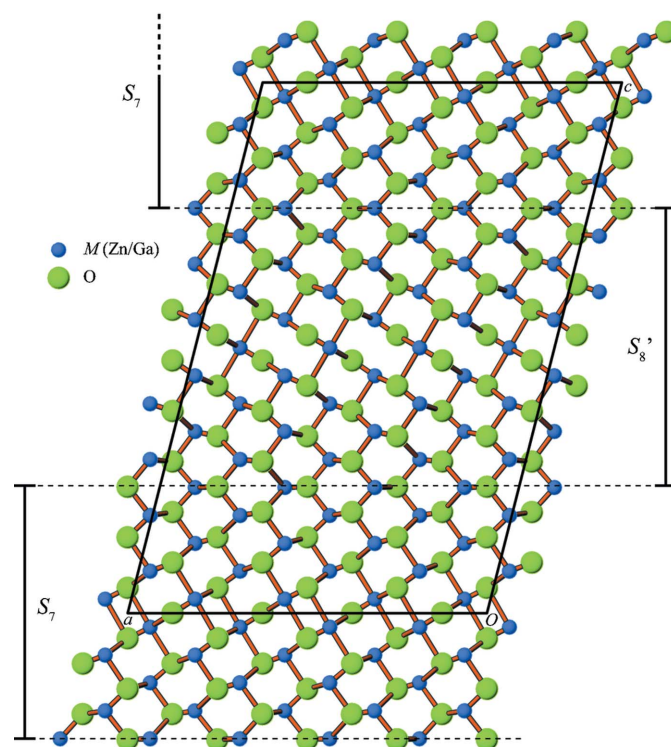


Figure 3
Hypothetical structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{15}$ projected along b .

4. Unified description of the homologous phases

$(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$

4.1. Idealized structures

For the unified description of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ an idealized structure model is defined in three-dimensional space, which is then transformed into a $(3+1)$ -dimensional model. Two cases of even and odd n are considered separately. The structure $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ in Fig. 4 is obtained by simply combining the halves of the unit cell in idealized structures of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_7$ proposed in our previous study (Michiue & Kimizuka, 2010). Fractional coordinates for ions are, however, based on the monoclinic unit cell and different from those of the orthorhombic structures. First, an orthogonal basis is used as for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ structures. All metal ions are on grid points $(x', z') = (i/8, j/(2n+5))$ on planes $y = 0$ and $y = 1/2$ (Fig. 4), where i and j are integers. Then, fractional coordinates (x, z) based on the monoclinic unit cell for these grid points are given as follows

$$(x, z) = \left(x' + \frac{3}{8}z', z' \right) = \left(\frac{(2n+5)i + 3j}{8(2n+5)}, \frac{j}{2n+5} \right). \quad (1)$$

The arrangement of oxygen ions is given in a similar manner to that used for metal ions. All O ions are put on the grid points $(x', z') = (i/8 + 1/16, (j+1/2)/(2n+7))$ on planes $y = 0$ and $y = 1/2$, and finally transformed as follows.

$$(x, z) = \left(x' + \frac{3}{8}z', z' \right) = \left(\frac{(2n+7)i + 3j + n + 5}{8(2n+7)}, \frac{2j+1}{2(2n+7)} \right). \quad (2)$$

Thus, the structure model in Fig. 4 is defined, which has the same symmetry as that of the real structure for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ of space group $C2/m$.

Considering the predicted structures for $n = 7$ in Fig. 3, an idealized model for odd n is given assuming that the metal ions are on the grid points $(x', z') = (i/8 + 1/16, (j+1/2)/(2n+5))$, and O ions are on $(x', z') = (i/8, j/(2n+7))$. Fractional coordinates based on the monoclinic unit cell for metal ions are given by

$$(x, z) = \left(x' + \frac{3}{8}z', z' \right) = \left(\frac{(2n+5)i + 3j + n + 4}{8(2n+5)}, \frac{2j+1}{2(2n+5)} \right). \quad (3)$$

Those for O ions are

$$(x, z) = \left(x' + \frac{3}{8}z', z' \right) = \left(\frac{(2n+7)i + 3j}{8(2n+7)}, \frac{j}{2n+7} \right). \quad (4)$$

The deviation of β from 90° in the monoclinic unit cell, that is θ in Fig. 4, is roughly given by $\tan^{-1}\{3a/[8(2n+5) \times 1.53]\}$. Strictly speaking, the model in Fig. 4 is different from the real

structure of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$. One of the nonequivalent metal ions on the boundary of S_6 and S_7 slabs is in a square-pyramidal coordination, that is $M17$ in the three-dimensional description. As seen in the previous section, a considerable amount of metal ions at the square-pyramidal site move to the neighbouring tetrahedral site, $M18$. Similar phenomena were observed for the metal sites on the mirror plane $z = 1/4$ in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ structures (Michiue *et al.*, 2008; Michiue & Kimizuka, 2010). Therefore, the same situation seems to occur in structures belonging to $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ as well as the $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ series. At the last part of this section, this problem is properly treated for the structure refinement in superspace in a similar way as for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue & Kimizuka, 2010).

4.2. Composite crystal model

Idealized structures presented in the preceding part are treated as composite crystals in this part. The composite crystal model consists of two subsystems, which are composed of metal and oxygen ions, respectively. In a usual $(3+1)$ -dimensional model an atomic domain is described by a straight

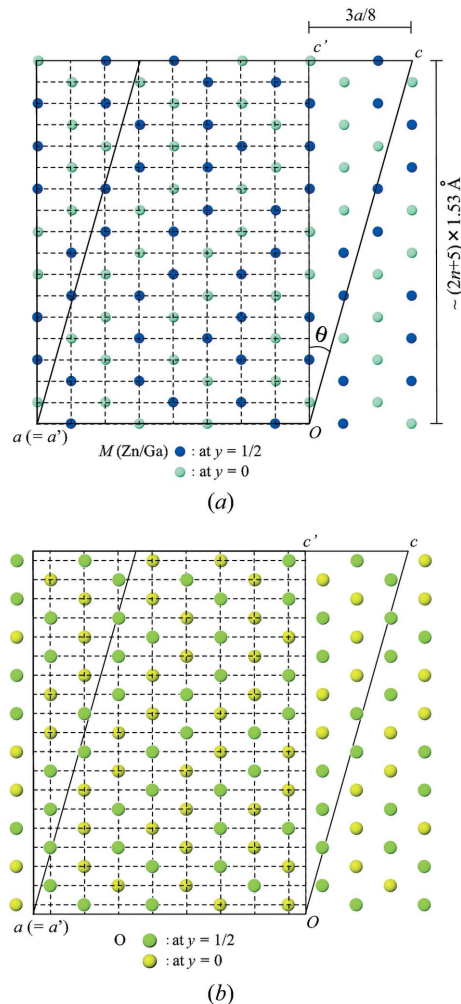


Figure 4 Positions of (a) metal (Zn/Ga) and (b) oxygen ions in an idealized structure for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ projected along **b**.

line at an initial stage, which is modified by introducing Fourier terms. However, such a (3 + 1)-dimensional model is available for neither of the two subsystems in the present case as mentioned for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue & Kimizuka, 2010). Instead, a specific structure model is built up in (3 + 1)-dimensional superspace and used as an initial model, in which atomic domains are not described by straight lines but zigzag lines with respect to x_1 .

When a composite crystal consists of two subsystems and each subsystem is modulated with the period of the other subsystem, the modulation wavevector of a subsystem is defined by the basic period of another subsystem in an intuitive setting, $\mathbf{q}_1 = \mathbf{c}_2^*$ and $\mathbf{q}_2 = \mathbf{c}_1^*$. The γ component of the modulation wavevector based on the first subsystem $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}_1^*$ is consequently $c_2^*/c_1^* = c_1/c_2$. However, in our previous study it was concluded that the intuitive setting is unsuitable for the unified description of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue & Kimizuka, 2010). As the same holds true for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$, non-intuitive settings were used for the discussion below.

As the first setting (type I setting), we take a basis $\mathbf{a}, \mathbf{b}, \mathbf{c}_1 = \mathbf{C}^n/(2n+5)$, where \mathbf{C}^n is the \mathbf{c} vector of a superstructure for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ in the three-dimensional description. A modulation wavevector is $\mathbf{q}_1 = \mathbf{C}^{n*} = \mathbf{c}_1^*/(2n+5)$ [that is, $\gamma = 1/(2n+5)$] for the first subsystem of metal ions, while $\mathbf{a}, \mathbf{b}, \mathbf{c}_2 = \mathbf{C}^n/(2n+7)$, and $\mathbf{q}_2 = \mathbf{C}^{n*}$ are taken for the second subsystem of O ions. The arrangement of metal and O ions on a plane $y =$

0 for a phase $n = 6$ is shown in Fig. 5. $2n + 5$ layers of metal ions are seen in a unit cell along \mathbf{c} , while $2n + 7$ O layers are contained in a unit cell. The structure is considered as a composite crystal, in which metal ions construct the first subsystem and the second subsystem consists of O ions. Atomic domains in both subsystems are, however, not described by the straight lines as mentioned below.

A superspace group of $C2/m(\alpha 0 \gamma)00$ is taken, of which the space group at the third section $t_0 = 0$ [modulo $1/(2n+5)$] is $C2/m$. A zigzag arrangement of metal ions is seen as indicated in Fig. 5, which is similar to the unit-cell twinning (Hyde *et al.*, 1979). However, the thickness of the neighbouring slabs are not identical in the present case. Metal ions indicated by Ps ($s = 1, 2, \dots, 17$) in the figure are at $z = s - 1$ in a sublattice based on \mathbf{c}_1 . These ions are allotted for the M1 and M2 ions in a (3 + 1)-dimensional model as projected on the x_3 - x_4 plane (Fig. 6a), which are at $x_3 = 0, 1, 2, \dots$ and extend along x_4 . A three-dimensional section defined by $t_0 (= x_4 - \gamma x_3) = 0$ is expressed by the horizontal line in the figure. P2 on the three-dimensional section is at $(x_3, x_4) = (1, 1/17)$ as indicated. The fractional coordinates (x_3, x_4) for Ps ($s = 1, 2, 3, \dots$) on the three-dimensional section are generally given by $(s - 1, (s - 1)\gamma) = (s - 1, (s - 1)/(2n + 5))$, which are translationally equivalent to positions on the x_4 axis $(0, (s - 1)/(2n + 5))$ as shown in Fig. 6(a). The fractional coordinates x of P1–P17 are given by equations (1), as indicated in Fig. 5(a). The positions of P1–P17 as given in Fig. 5(a) and Fig. 6(a) are plotted on the

x_1 - x_4 plane in Fig. 6(b). An asymmetric zigzag function is suitable for the description of such an arrangement, which is replaced by the combination of sawtooth functions (Fig. 6c) in refinements using JANA2006. Consequently, an atomic domain of the metal ion is divided into two parts, M1 and M2. M1 with a sawtooth function defined by the center $(x_1^0, x_2^0, x_3^0, x_4^0) = (3/8, 0, 0, 0)$, the width of an occupation domain $\Delta = (n + 3)/(2n + 5)$, and the amplitude $V_{x1} = 3(n + 3)\Delta/8$ corresponds to ions P1–P5, and P14–P17 in three-dimensional space. Another part M2 for P6–P13 is defined by the center $(x_1^0, x_2^0, x_3^0, x_4^0) = (3/8, 0, 0, 1/2)$, the width of an occupation domain $\Delta = (n + 2)/(2n + 5)$, and the amplitude $V_{x1} = -3(n + 2)\Delta/8$. Parameters for O ions were obtained in the same manner. (It would be easier to use type (II) setting for the derivation of parameters of the O ion, because an atomic domain of the O ion extends along x_4 in type (II) setting as explained in the following para-

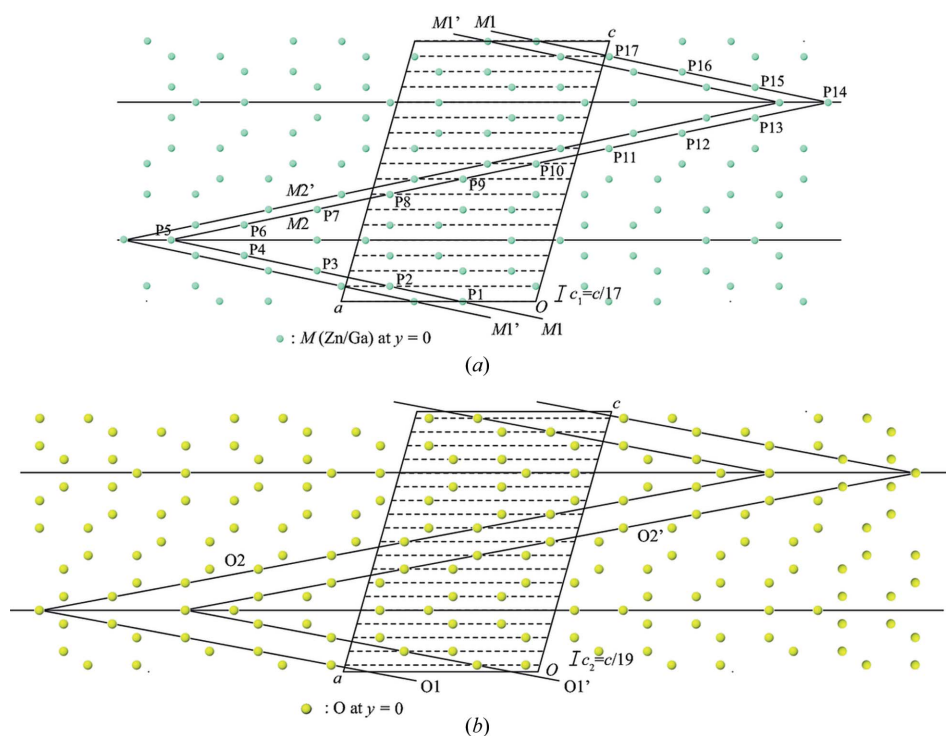


Figure 5 Arrangement of (a) metal and (b) oxygen ions on the $y = 0$ plane in the idealized structure model for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$. Ps is the metal site. Correspondence between metal sites Ps and Mn for the real structure in Fig. 1 is given as a list in the supplementary material. M1, M2, O1 and O2 correspond to atomic domains in a (3 + 1)-dimensional description. M1', M2', O1' and O2' are related by the inversion center to M1, M2, O1 and O2, respectively.

Table 4

Crystallographic data and structural parameters for the unified model of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ in $(3+1)$ -dimensional superspace.

Type (I):	Monoclinic, $C2/m(\alpha 0 \gamma)00$ $a \approx 19.7, b \approx 3.25, c_1 \approx 1.53/\cos \theta$ (Å), $\beta = 90 + \theta$ (°), $[\tan \theta \approx 3a/(8(2n+5) \times 1.53)]$, $c_2 = (2n+5)c_1/(2n+7)$, $\mathbf{q}_1 = \mathbf{c}_1^*/(2n+5)$, $\gamma = 1/(2n+5)$
Type (II):	Monoclinic, $C2/m(\alpha 0 \gamma)00$ $a \approx 19.7, b \approx 3.25, c_1 \approx 1.38/\cos \theta$ (Å), $\beta = 90 + \theta$ (°), $[\tan \theta \approx 3a/(8(2n+5) \times 1.53)]$, $c_2 = (2n+7)c_1/(2n+5)$, $\mathbf{q}_1 = \mathbf{c}_1^*/(2n+7)$, $\gamma = 1/(2n+7)$
Type (III):	Monoclinic, $C2/m(\alpha 0 \gamma)00$ $a \approx 19.7, b \approx 3.25, c_0 \approx 1.46/\cos \theta$ (Å), $\beta = 90 + \theta$ (°), $[\tan \theta \approx 3a/(8(2n+5) \times 1.53)]$, $c_1 = (2n+6)c_0/(2n+5)$, $c_2 = (2n+6)c_0/(2n+7)$, $\mathbf{q}_0 = \mathbf{c}_0^*/(2n+6)$, $\gamma = 1/(2n+6)$

Model 1: for even n at $t_0 = 0$ (modulo γ), and for odd n at $t_0 = \gamma/2$ (modulo γ)

	x_1^0	x_2^0	x_3^0	x_4^0	Δ	V_{x1}
Subsystem 1						
M1	3/8	0	0	0	$(n+3)/(2n+5)$	$3(n+3)\Delta/8$
M2	3/8	0	0	1/2	$(n+2)/(2n+5)$	$-3(n+2)\Delta/8$
Subsystem 2						
O1	7/8	0	1/2	0	$(n+4)/(2n+7)$	$3(n+4)\Delta/8$
O2	7/8	0	1/2	1/2	$(n+3)/(2n+7)$	$-3(n+3)\Delta/8$

$V_{x2} = V_{x3} = 0$ for all sites. In type (II) setting, O1 and O2 are allotted for the first subsystem, and M1 and M2 are allotted for the second one.

Model 2: for odd n at $t_0 = 0$ (modulo γ), and for even n at $t_0 = \gamma/2$ (modulo γ)

	x_1^0	x_2^0	x_3^0	x_4^0	Δ	V_{x1}
Subsystem 1						
M1	7/8	0	1/2	0	$(n+3)/(2n+5)$	$3(n+3)\Delta/8$
M2	7/8	0	1/2	1/2	$(n+2)/(2n+5)$	$-3(n+2)\Delta/8$
Subsystem 2						
O1	3/8	0	0	0	$(n+4)/(2n+7)$	$3(n+4)\Delta/8$
O2	3/8	0	0	1/2	$(n+3)/(2n+7)$	$-3(n+3)\Delta/8$

$V_{x2} = V_{x3} = 0$ for all sites. In type (II) setting, O1 and O2 are allotted for the first subsystem, and M1 and M2 are for the second one. W matrices (van Smaalen, 1991) are

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 2 \\ 0 & 0 & 0 & 1 \end{pmatrix} \text{ for type (I) setting, } \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & -2 \\ 0 & 0 & 0 & 1 \end{pmatrix} \text{ for type (II) setting, and}$$

$$W_1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \end{pmatrix} \text{ and } W_2 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{pmatrix} \text{ for type (III) setting,}$$

$$\text{where } \begin{pmatrix} \mathbf{a}_1^* \\ \mathbf{b}_1^* \\ \mathbf{c}_1^* \\ \mathbf{q}_1 \end{pmatrix} = W_1 \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}_0^* \\ \mathbf{c}_0^* \\ \mathbf{q}_0 \end{pmatrix} \text{ and } \begin{pmatrix} \mathbf{a}_2^* \\ \mathbf{b}_2^* \\ \mathbf{c}_2^* \\ \mathbf{q}_2 \end{pmatrix} = W_2 \begin{pmatrix} \mathbf{a}^* \\ \mathbf{b}_0^* \\ \mathbf{c}_0^* \\ \mathbf{q}_0 \end{pmatrix}.$$

graph.) Thus, a structure model is established in $(3+1)$ -dimensional space, that is model 1 in Table 4. Further, another $(3+1)$ -dimensional model (model 2 in Table 4) is built up considering the arrangement of metal and O ions on a $y = 0$ plane for phase $n = 7$ in Fig. 4. Thus, two types of the model are given as in the case of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$. These models were given by taking the three-dimensional section $t_0 = 0$ (modulo

γ); one is for even n (model 1), and another is for odd n (model 2). Each subsystem contains two ions, and fractional coordinates $x_1 - x_4$ of the metal ions for odd n are equal to those of the O ions for even n . Structure parameters of model 1 are equal to those of model 2, while the origin of the former is shifted by $\mathbf{r}_1 = (x_1, x_2, x_3) = (\frac{1}{2}, 0, \frac{1}{2})$. Considering the correction of $\mathbf{q} \cdot \mathbf{r}_1 = \gamma/2$, the three-dimensional section after the origin shift should be $t_0 = \gamma/2$. Thus, we can take model 1 as a common structure model for both even and odd n , although the three-dimensional section $t_0 = \gamma/2$ (modulo γ) should be taken for odd n . Also, model 2 can be used for even n taking the three-dimensional section $t_0 = \gamma/2$ (modulo γ). It is noted that a single atomic domain described by an asymmetric zigzag function is divided into two parts of the sawtooth function in refinement for each of the metal and oxygen ions, which is different from the case in $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue & Kimizuka, 2010).

When O ions are taken for the first subsystem [type (II) setting], a basis set $\mathbf{a}, \mathbf{b}, \mathbf{c}_1 = \mathbf{C}^n/(2n+7)$ and a modulation wavevector $\mathbf{q}_1 = \mathbf{C}^{n*} = \mathbf{c}_1^*/(2n+7)$ [that is, $\gamma = 1/(2n+7)$] are taken for the first subsystem, while the basis of the second subsystem is $\mathbf{a}, \mathbf{b}, \mathbf{c}_2 = \mathbf{C}^n/(2n+5)$, and $\mathbf{q}_2 = \mathbf{C}^{n*}$. In this setting, the O ions extend along x_4 , and the metal ions extend along the direction $(x_3, x_4) = (2, 1)$ (Fig. 7a). A superspace group is $C2/m(\alpha 0 \gamma)00$ [$\gamma = 1/(2n+7)$] in this case too. Structural parameters for this setting are the same as those in Table 4, although the O1 and O2 are allotted for the first subsystem and the M1 and M2 for the second subsystem. Furthermore, an intermediate setting [type (III) setting] is also possible, as for the series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue & Kimizuka, 2010). A unit basis set $\mathbf{a}, \mathbf{b}, \mathbf{c}_0 = \mathbf{C}^n/2(n+3)$ with a modulation wavevector $\mathbf{q}_0 = \mathbf{C}^{n*} = \mathbf{c}_0^*/2(n+3)$ is taken for a

void zeroth subsystem, which is the subsystem containing no atom. A unit basis set $\mathbf{a}, \mathbf{b}, \mathbf{c}_1 = \mathbf{C}^n/(2n+5)$ with a modulation wavevector $\mathbf{q}_1 = \mathbf{C}^{n*}$ is taken for the first subsystem of metal ions, and $\mathbf{a}, \mathbf{b}, \mathbf{c}_2 = \mathbf{C}^n/(2n+7)$, and $\mathbf{q}_2 = \mathbf{C}^{n*}$ are for the second subsystem of O ions. In this setting the metal ions extend along the direction $(x_3, x_4) = (1, 1)$, while the O ions along $(x_3, x_4) = (-1, 1)$ (Fig. 7b). A superspace group $C2/m(\alpha 0 \gamma)00$ [$\gamma = 1/$

$2(n + 3)]$ is used in this case, and structural parameters for this setting are the same as those in Table 4. Used bases for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ in the three settings are illustrated in direct and reciprocal spaces (Fig. 8).

4.3. Superspace description of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$

Refinements of real structures in the homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ are carried out based on the $(3 + 1)$ -dimensional model derived in the preceding part. Deviations from the idealized structure in Fig. 4 are, in principle, corrected by additional Fourier terms of modulation functions in $(3 + 1)$ -dimensional refinements. The validity of the method is demonstrated by the structure refinement for a phase of $n = 6$ in the homologous series. Using the settings and models

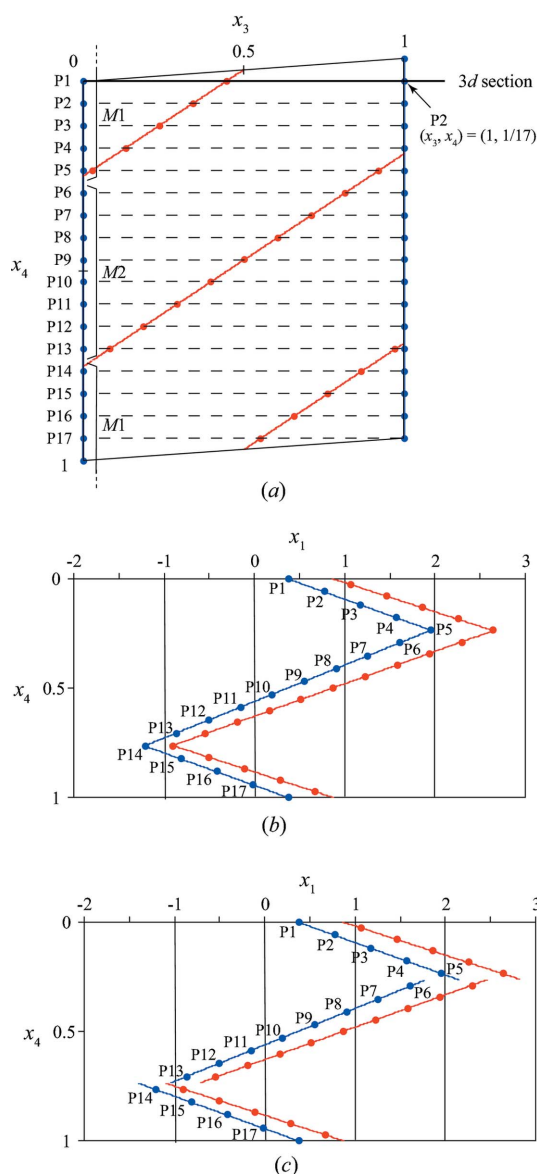


Figure 6 Projection of metal and oxygen ions of a $(3 + 1)$ -dimensional model of $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ on (a) the x_3 - x_4 plane, (b) the x_1 - x_4 plane by asymmetric zigzag functions, and (c) the x_1 - x_4 plane by sawtooth functions.

described in the last section, there are six options for the possible model and setting, that is the combination of the two models (model 1 and 2) and three types of setting [types (I)–(III)]. As all of the six options are essentially equivalent to each other, only one set, model 1 with type (I) setting, is presented.

First, it is necessary to modify the $(3 + 1)$ -dimensional model in Fig. 5. One of the nonequivalent metal sites, P5, in the model is in the square-pyramidal coordination, which is a rather uncommon environment for metal ions. Structure refinement in three-dimensional space revealed that this metal site, $M17$, is not fully occupied, and a displaced position $M18$ was introduced for the accommodation of metal ions moving away from the $M17$ site. The $M17$ was treated as a part of $M1$ in the idealized model in the previous section. However, it is difficult to deal with $M17$ and $M18$ sites as part of $M1$ in the $(3 + 1)$ -dimensional model. Thus, $M17$ and $M18$ are separated from the atomic domain $M1$ and treated as independent sites $M1a$ and $M1b$. Parameters for the O ions of the second

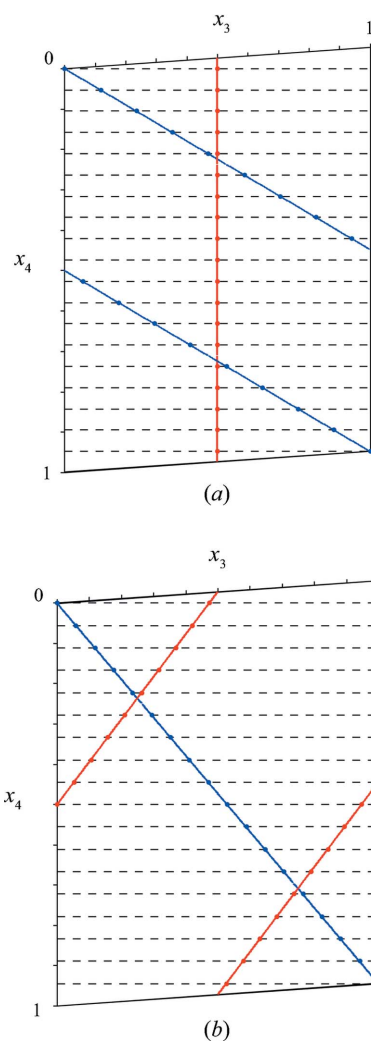


Figure 7 Projection of atomic domains for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ on the x_3 - x_4 plane in the setting (a) type (II) and (b) type (III). Metal and oxygen ions are blue and red lines, respectively.

subsystem in Table 4 are used for the initial model without modification.

The atomic domain for P5 (*M17*) is separated from the *M1*, and treated as an independent site *M1a* using the crenel function with $\Delta = 1/17$ [$\Delta = 1/(2n + 5)$ for general n]. Consequently, the center of the *M1* shifts to $(x_1^0, x_2^0, x_3^0, x_4^0) = (3/17, 0, 0, -1/34)$, as shown in Fig. 9(a). The width Δ and the amplitude V_{x1} of the sawtooth function are reduced, while the slope $V_{x1}/\Delta = 3(n + 3)/8$ is unchanged. Another occupation domain *M1b* with $\Delta = 1/17$ is allotted for the *M18* site. A constraint condition was imposed on the occupation factors so

that $Occ[M1a] + Occ[M1b]$ is unity. Atomic domains of metal and oxygen ions are projected on the x_1-x_4 (Fig. 9a) and x_3-x_4 (Fig. 9b) planes. Parameters in Table 5 are identical for all types of the setting, while metal sites are taken for the second subsystem and the oxygen ions are for the first subsystem in type II setting. Results of the refinement with 179 parameters are summarized in Table 6, which should be equivalent to those from the three-dimensional refinement if all of the refinable parameters were refined. It is noted that adequate results are obtained from the (3 + 1)-dimensional model despite the less parameters. The final CIF can be downloaded from the Bilbao Incommensurate Structures Database, <http://158.227.21.14/incstrdb/>, under record number 6272EzStLP.

5. Concluding remarks

The structure of $(Ga_2O_3)_2(ZnO)_{13}$ is constructed by combining halves of the unit cell of $Ga_2O_3(ZnO)_6$ and

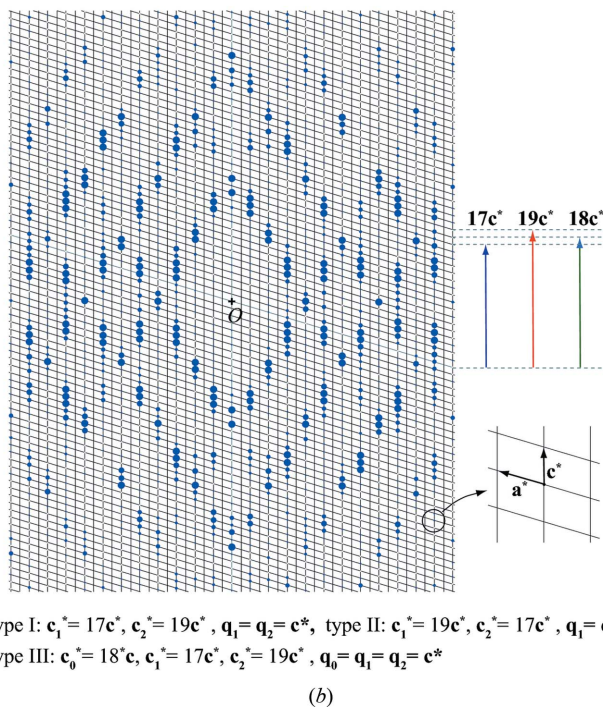
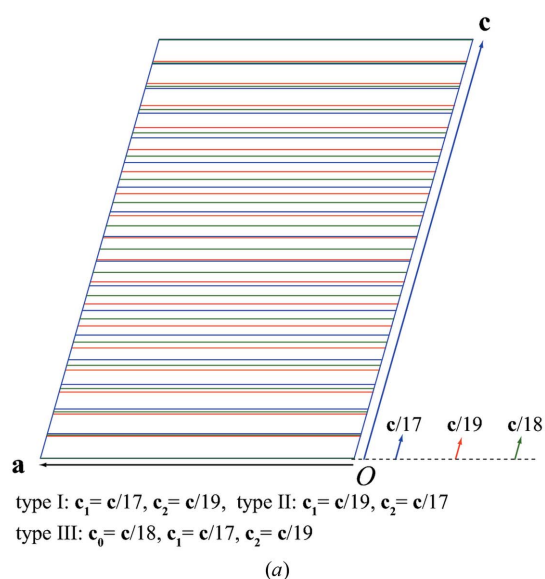


Figure 8
 Bases for $(Ga_2O_3)_2(ZnO)_{13}$ in the three settings illustrated in (a) direct and (b) reciprocal space. The diffraction pattern of the $h0l$ layer is shown in reciprocal space.

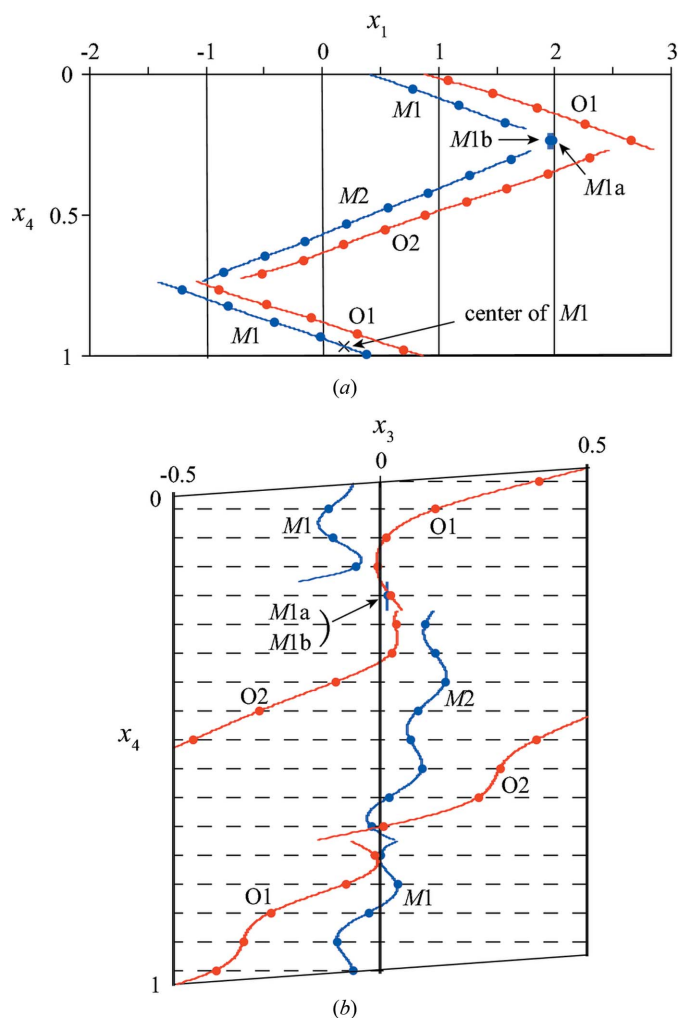


Figure 9
 Projection of metal and oxygen ions for $(Ga_2O_3)_2(ZnO)_{13}$ on (a) x_1-x_4 and (b) x_3-x_4 planes.

Table 5
Modified structure parameters for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$ in model 1.

	x_1^0	x_2^0	x_3^0	x_4^0	Δ	V_{x1}
Subsystem 1						
M1	0.1829 (3)	0	-0.1054 (8)	-0.03561 (5)	8/17	27/17
M1a	1.97979 (18)	0	0.012 (3)	0.23598 (17)	1/17	
M1b	1.95398 (10)	1/2	0.0088 (14)	0.23581(8)	1/17	
M2	0.38666 (11)	0	0.0873 (3)	0.505138 (19)	8/17	-24/17
Subsystem 2						
O1	0.8835 (10)	0	0.428 (2)	-0.00378 (13)	10/19	75/38
O2	0.8865 (8)	0	0.566 (2)	0.50350 (12)	9/19	-243/152

The crenel function is used for the occupation function of M1a, M1b. x_4^0 is given by $1/34 + x_3^0/17, 1/2 + x_3^0/17, -1/38 + x_3^0/19, 9/19 + x_3^0/19$ for M1, M2, O1 and O2, respectively, so that the center of the atomic domain is constant with respect to z . x_4^0 is given by $4/17 + x_3^0/17$ for M1a and M1b, so that the three-dimensional section goes through the center of the atomic domain. The sum of the occupation factors at M1a and M1b is fixed to unity. The occupation ratio Ga/Zn is fixed to 4/13 for all metal sites. In the type (II) setting, O1 and O2 are allotted for the first subsystem, and M1 and M2 are for the second one. Coefficients of additional Fourier series are given in the CIF. $a = 19.66$ (4), $b = 3.2487$ (5) Å, $\beta = 105.90$ (10) $^\circ$ for all settings of types (I)–(III), and $c_1 = 1.6065$ (12), $c_2 = 1.4374$ (11) Å, $\mathbf{q}_1 = \mathbf{c}_1^*/17$ for type (I) setting, $c_1 = 1.4374$ (11), $c_2 = 1.6065$ (12) Å, $\mathbf{q}_1 = \mathbf{c}_1^*/19$ for type (II) setting, $c_0 = 1.5172$ (11), $c_1 = 1.6065$ (12), $c_2 = 1.4374$ (11) Å, $\mathbf{q}_0 = \mathbf{c}_0^*/18$ for type (III) setting.

Table 6
Results of the refinement for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{13}$.

	Three-dimensional	(3 + 1)-dimensional
Independent /observed [$I_o > 2\sigma(I_o)$] reflections	7763/4676	7763/4676
Number of parameters	225	179
$R_{\text{obs}}(F)/wR_{\text{all}}(F^2)$		
All	0.0610/0.1949	0.0656/0.2022
Main reflections	–	0.0717/0.1679
Satellites of order 1	–	0.0733/0.2155
2	–	0.0767/0.1541
3	–	0.0597/0.1419
4	–	0.0567/0.1210
S	2.88	2.98

$\text{Ga}_2\text{O}_3(\text{ZnO})_7$ in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue *et al.*, 2008). A homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ was derived and a unified structure model for the series was presented using the (3 + 1)-dimensional superspace description. The structure model was given as the commensurate composite crystal, in which displacive modulations of ions were described by asymmetric zigzag functions with large amplitudes with respect to x_1 . These characters are similar to those seen in $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ (Michiue & Kimizuka, 2010) and the lillianite series (Elcoro *et al.*, 2008). The asymmetric zigzag function is replaced by the combination of sawtooth functions in the model for structure refinements. The validity of the model was confirmed by refinements for phase $n = 6$ in the series, although the (3 + 1)-dimensional model was modified before being used in refinements; part of an atomic domain for the metal ion was separated from the rest and treated as independent sites. Reliability factors from the refinements were adequately close to those from the third refinements even when the number of parameters was less than the maximum permitted.

A superspace model including both structures of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ and $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ was unavailable as far as we tried. A serious problem arises from the fact that the

atomic domains in the model for $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ are described by the asymmetric zigzag function, while those for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are given by the normal (*i.e.* symmetric) zigzag function. It is expected that structural variations in connection with the homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ are abundant and extensive. For example, a simple sequence of two unit cells for $m = n$ and $m = n + 1$ of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ gives another type of long-period structure. The unit cell consisting of a sequence $S_n-S'_n-S_{n+1}-S'_{n+1}$ has mirror planes normal to \mathbf{c} , forming an orthorhombic structure. A chemical composition for this hypothetical structure is also $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$. Thus, various hypothetical structures are derived by

changing the sequence mode. So far as the number of S_n (and S'_n) slabs contained in a structure is the same to the number of S_{n+1} (and S'_{n+1}), the chemical composition is always $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$, which means the possibility of polytypes for each member of the homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$. Since $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ has been found to have promising properties as a new transparent conducting oxide and also as a thermoelectric material (Michiue *et al.*, 2011), such material design of the homologous series $(\text{Ga}_2\text{O}_3)_2(\text{ZnO})_{2n+1}$ can lead to further attractive development of the physical properties also.

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