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Structure analysis of new homologous compounds $Ga_2O_3(ZnO)_m$ (m = integer) by high-resolution analytical transmission electron microscopy

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Abstract

The crystal structure of a new homologous compound series, $Ga_2O_3(ZnO)_m$ (m = integer), is determined by high-resolution lattice imaging and high spatial resolution energy-dispersive X-ray spectroscopy (EDS) analysis in a field-emission analytical transmission electron microscope. This work was carried out mainly on the compound with m = 9 (digallium nonazinc dodecaoxide), which belongs to the orthorhombic system and has lattice constants a_o = 0.33, b_o = 2.0 and c_o = 3.4 nm. From the extinction rules three possible space groups are selected and from them a unique space group is assigned as noncentrosymmetric $Cmc2_1$ (No. 36) on the basis of structural requirements. $Ga_2O_3(ZnO)_m$ is a layered structure consisting of Ga–O and $m + 1$ Ga/Zn–O layers stacked alternately along the c axis. It is shown that the structure of $Ga_2O_3(ZnO)_m$ differs from that of $M_2O_3(ZnO)_m$ (M = In, Fe; m = integer) reported previously. In $Ga_2O_3(ZnO)_m$ the Ga atoms occupy the tetrahedral sites in the Ga–O layers, whereas the M atoms in the M–O layers occupy the octahedral sites in $M_2O_3(ZnO)_m$ (M = In, Fe).

1. Introduction

In a study of the phase diagrams of the In_2O_3–M_2O_3–ZnO (M = In, Fe, Ga) systems (Kimizuka *et al.*, 1993, 1995; Nakamura *et al.*, 1990, 1991, 1993), new homologous compounds having the chemical formula $M_2O_3(ZnO)_m$ (M = In, Fe, Ga; m = integer) have been found. Among them, the structures of $M_2O_3(ZnO)_m$ (M = In, Fe) have been studied by X-ray diffraction and high-resolution transmission electron microscopy (Hiramatsu *et al.*, 1997; Kimizuka *et al.*, 1993; Li *et al.*, 1997; Li, Bando, Nakamura, Onoda & Kimizuka, 1998; Li, Bando, Nakamura & Kimizuka, 1998; Nakamura *et al.*, 1990; Ohta *et al.*, 1996). It was reported that $M_2O_3(ZnO)_m$ (M = In, Fe) have an $LuFeO_3(ZnO)_m$-type structure consisting of MO_2^- (M–O) and $MZn_mO_{m+1}^+$ (M/Zn–O) layers stacked alternately along the c axis. The M ions in the M–O layer occupy the octahedral sites formed by the close-packed O atoms, while M and Zn in the M/Zn–O layers occupy the tetrahedral or trigonal-bipyramidal sites. These structural considerations were used to explain the failure of attempts to synthesize the compounds $Al_2O_3(ZnO)_m$ in the In_2O_3–Al_2O_3–ZnO system (Nakamura *et al.*, 1993), as Al was considered to be too small to occupy the octahedral site. Since the ionic radius of Ga is between those of Al and Fe, it is doubtful whether Ga can occupy the octahedral site and whether $Ga_2O_3(ZnO)_m$ adopts an $LuFeO_3(ZnO)_m$-type structure. Although unit cells for $Ga_2O_3(ZnO)_m$ different from those of the $LuFeO_3(ZnO)_m$-type compounds were suggested by X-ray diffraction (Kimizuka *et al.*, 1995), the detailed atomic arrangement in $Ga_2O_3(ZnO)_m$ remains unknown.

It is well known that high-resolution electron microscopy is a useful method for crystal structure analysis based on the direct observation of atomic arrangements. This method is very powerful in the present case since the synthesized samples of $Ga_2O_3(ZnO)_m$ are in the form of fine grains several µm in diameter. Since Ga and Zn are neighboring elements in the periodic table, their image contrasts may not be different enough to be distinguished from each other. The use of an analytical electron microscope allows the probable ordering of the Ga ions to be checked by fine-region composition analysis (Bando, 1995).

In this paper the crystal structure analysis of $Ga_2O_3(ZnO)_m$ by high-resolution analytical transmission electron microscopy is reported. It is shown that $Ga_2O_3(ZnO)_m$ belongs to the orthorhombic crystal system and has a structure which consists of Ga–O and (m + 1) Ga/Zn–O layers stacked alternately along the c_o axis.

2. Experimental

Solid-state reactions were used for the sample preparations. Prior to mixing, powders of Ga_2O_3 and ZnO (99.9%) were preheated at about 1273 K for 1 d. Stoichiometric proportions of these starting powders were weighed and mixed in an agate mortar. Each mixture was sealed in a Pt tube and heated at temperatures above 1623 K for about 7 d. The samples were then rapidly cooled to room temperature. Evaporation of the samples during the heat treatment was negligible. Under these preparation conditions compounds with m ranging from 7 to 16 were synthesized, and $Ga_2O_3(ZnO)_9$ and $Ga_2O_3(ZnO)_{13}$ were observed in the present study.

For the electron-microscope observations the samples prepared as above were crushed in an agate mortar. They were then dispersed onto a holey carbon grid using a CCl_4 solution. Electron diffraction patterns, lattice images and EDS analysis were carried out using a JEM-3000F analytical electron microscope, operated at an accelerating voltage of 300 kV. For EDS analysis, the electron beam was focused to about 0.5 nm in diameter; it takes approximately 20 s to collect one spectrum.

3. Results and discussion

Fig. 1 shows the electron diffraction patterns of $Ga_2O_3(ZnO)_9$ corresponding to the reciprocal-lattice sections $\mathbf{a}_o^* - \mathbf{b}_o^*$ (Fig. 1*a*), $\mathbf{b}_o^* - \mathbf{c}_o^*$ (Fig. 1*b*), $\mathbf{a}_o^* - \mathbf{c}_o^*$ (Fig. 1*c*) and $(\mathbf{a}_o^* + \mathbf{b}_o^*) - \mathbf{c}_o^*$ (Fig. 1*d*). These electron diffraction patterns can be indexed using an orthorhombic unit cell with $a_o = 0.33$, $b_o = 2.0$ and $c_o = 3.4$ nm, which is the same as that suggested by X-ray diffraction. The conditions limiting the possible diffraction spots are hkl: $h + k = 2n$ and $h0l$: $l = 2n$ ($h = 2n$), which lead to the possible space groups $Cmc2_1$ (No. 36), $C2cm$ (No. 40), and $Cmcm$ (No. 63).

The lattice images corresponding to the diffraction pattern of Fig. 1(*b*) are shown in Figs. 2(*a*) and (*b*) with low and high magnifications, respectively. In Fig. 2(*a*), wedge-shaped image contrast was observed. It should be pointed out that the image contrast changed drastically from the thin area (the left edge) to the thick area (the right-hand side). The wedge-shaped contrast can be observed most clearly in the areas about 2 cm away from the left edge. The axis of the wedge is normal to the c_o axis of the crystal and its apex angle is about 60°. It should also be pointed out that the neighboring wedge-shaped tips have the same contrast in the thin areas but different contrast in the thick areas. Obviously, this arises from dynamic scattering effects. In Fig. 2(*b*), based on our experience of structural studies of the compounds $In_2O_3(ZnO)_m$ (Li *et al.*, 1997; Li, Bando, Nakamura, Onoda & Kimizuka, 1998) and $Fe_2O_3(ZnO)_m$ (Li, Bando, Nakamura & Kimizuka, 1998) and the simulation results to be illustrated later, the dark dots are believed to correspond to the metal-atom positions. For convenience, we refer to the dark

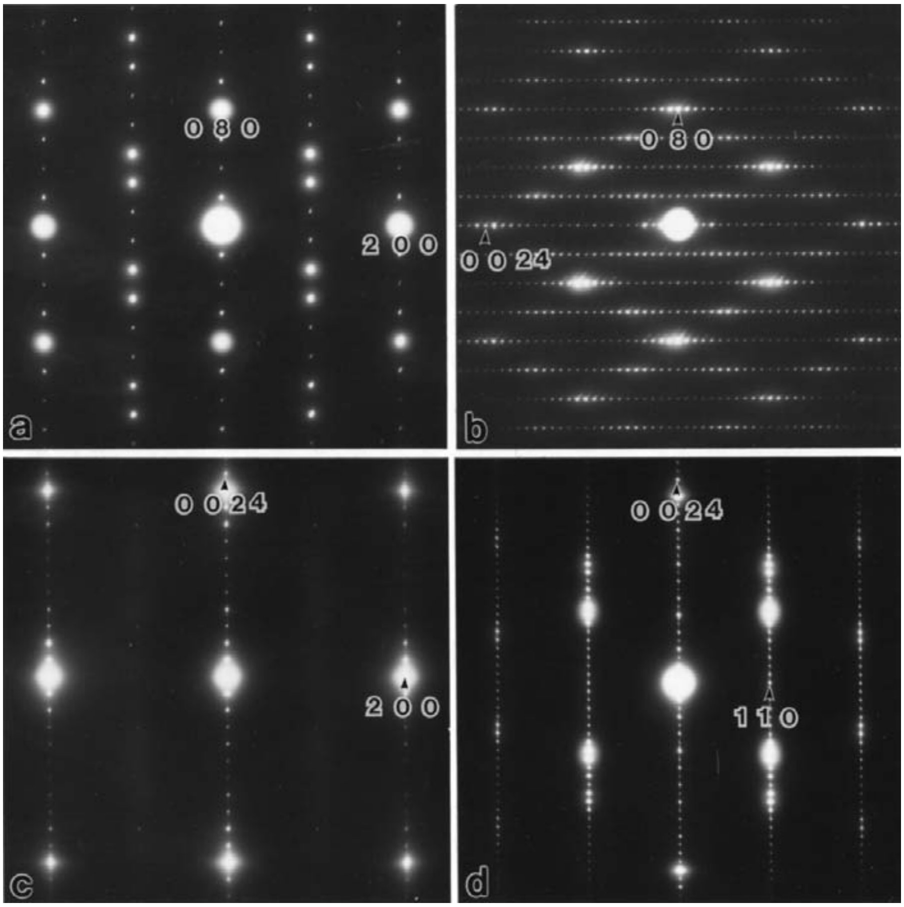

Fig. 1. Electron diffraction patterns of $Ga_2O_3(ZnO)_9$, corresponding to (*a*) $\mathbf{a}_o^* - \mathbf{b}_o^*$, (*b*) $\mathbf{b}_o^* - \mathbf{c}_o^*$, (*c*) $\mathbf{a}_o^* - \mathbf{c}_o^*$, and (*d*) $(\mathbf{a}_o^* + \mathbf{b}_o^*) - \mathbf{c}_o^*$ reciprocal-lattice sections. The appearance of forbidden $00l$ ($l = 2n + 1$) spots in (*b*) and (*d*) is the result of dynamic scattering effects.

dots located approximately in one line normal to the c_o axis as one layer. The contrast of the dark dots located in the tip of the wedge-shaped lattice is a little darker and they separate from their surrounding dots more than the others. In addition, composition analysis (described later) showed the enrichment of Ga atoms in these layers. Therefore, these layers are indicated as Ga–O while the others are indicated as Ga/Zn–O. There are ten Ga/Zn–O layers sandwiched by two neighboring Ga–O layers.

It is very reasonable to believe that the Ga/Zn–O layers have a crystal structure analogous to that of wurtzite-type ZnO for the following two reasons. First, ZnO contributes a very high weight in the chemical formula of $Ga_2O_3(ZnO)_9$. Second, the image contrast of Ga/Zn–O in Fig. 2(*b*) is very similar to that of wurtzite-type ZnO observed along its [100] orientation. This structural consideration can be used to reduce the number of possible space groups. First, we consider the cases of *C*2*cm* (No. 40) and *Cmcm* (No. 60). Their common symmetries include a mirror plane normal to the *c* axis and a twofold rotation along the a_o axis. The relative positions of these two symmetries along the c_o axis is a shift by $\mathbf{c}_o/4$ according to *International Tables*

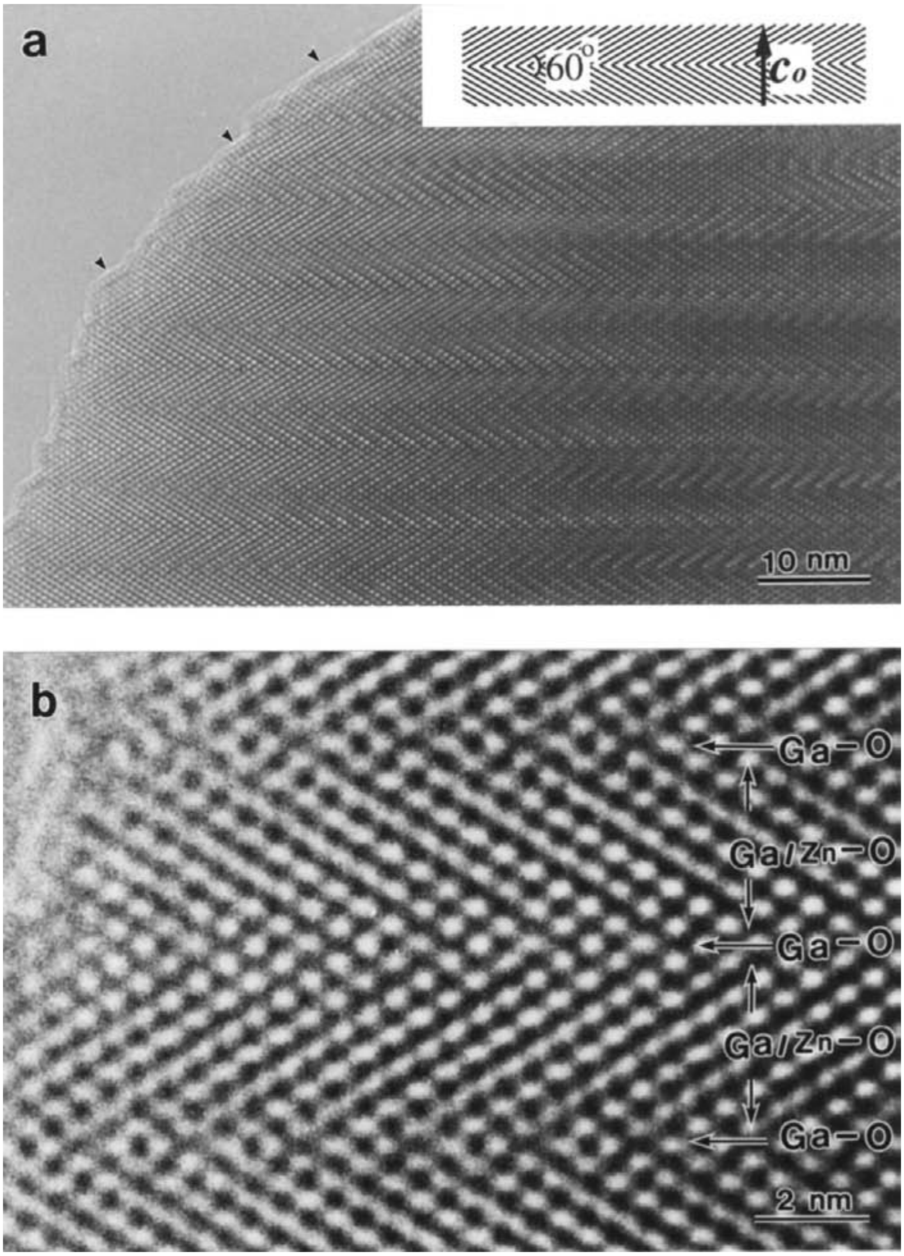

Fig. 2. Images of $Ga_2O_3(ZnO)_9$ at (*a*) low and (*b*) high magnifications. The images were taken with the incident electron beam parallel to the [100] direction.

for Crystallography (Vol. A, 1989). From the image shown in Fig. 2(*b*), it is obvious that the mirror plane coincides with the Ga–O layer. Therefore, the twofold rotation is located in the center of the Ga/Zn–O layer blocks, which are believed to have an analogous structure to that of wurtzite-type ZnO. Since there is no twofold rotation symmetry operation in wurtzite-type ZnO, the space groups *C2cm* (No. 40) and *Cmcm* (No. 60) should be rejected. The space group $Cmc2_1$ (No. 36) has no twofold rotation symmetry along the [100] orientation and is compatible with the wurtzite-type ZnO structure of the Ga/Zn–O layer.

Fig. 3(*a*) shows a structural model of $Ga_2O_3(ZnO)_9$. The axes of the present orthorhombic unit cell are represented by a_o, b_o, and c_o. The cell can be divided into lower and upper parts. These two parts are related to each other by a 2_1 symmetry operation along the c_o axis. Since it is proposed that the coordinates of atoms along the a_o axis are either 0 or $\frac{1}{2}$, this 2_1 symmetry operation is the same function as that of the c_o glide mirror normal to the b_o axis. From the discussion above, it is clear that an illustration of only the lower half is enough for an understanding of the model. In the lower half, the atomic arrangement is based on that of wurtzite-type ZnO, where the Zn atoms occupy the tetrahedral sites between the O atoms. The c_{ZnO} axis of ZnO forms an angle of about 30° with respect to the c_o axis. Some metal and O atoms can be sandwiched by the two dashed lines normal to the c_o axis as shown in the top part of Fig. 3. For convenience, we propose that these atoms form a Ga/Zn–O layer. First, 12 Ga/Zn–O layers were introduced in the lower half. The ratio of metal to O atoms is 1:1, which is different from the chemical formula $Ga_2O_3(ZnO)_9$ of this compound. To solve this problem, the metal atoms in the bottom Ga/Zn–O layer were deleted. Then the ratio Ga/Zn:O is 11:12, which is in agreement with the chemical formula. In the top Ga/Zn–O layer of the lower half, the sites of the metal atoms were proposed to be occupied completely by Ga atoms to correspond to the tip layer of the wedge-shaped lattice. The upper half can be obtained by the 2_1 symmetry operation on such a lower half. This leaves the lower and upper parts connected to each other by two O-atom layers, the possibility of which is very low from a crystallographic point of view. Therefore, it is proposed that the Ga atoms shift from their original tetrahedral sites to the center of these two neighboring O-atom layers, forming a GaO_2^- (Ga–O) layer. There are ten Ga/Zn–O layers sandwiched by two neighboring Ga–O layers. The atomic ratio of Ga:Zn in the Ga/Zn–O layer

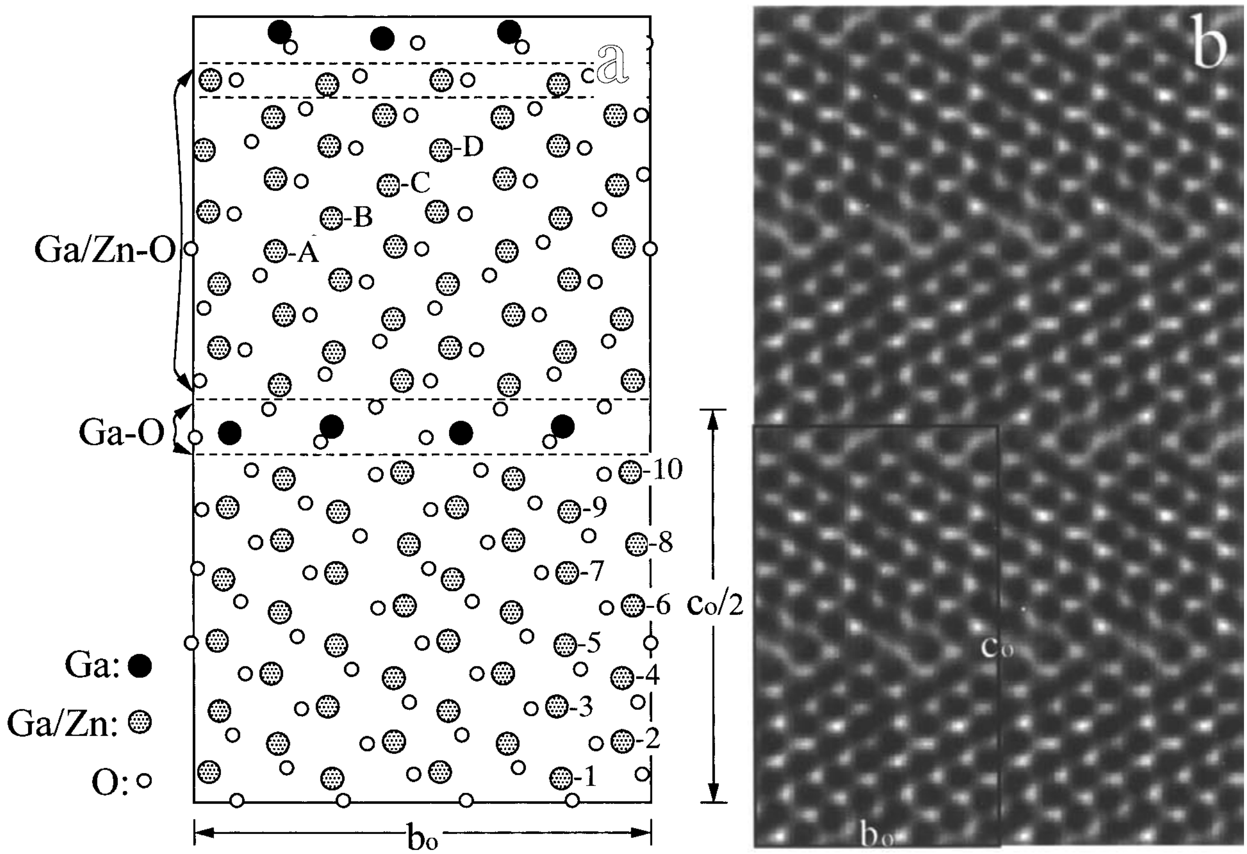

Fig. 3. (*a*) A crystal structure model and (*b*) the corresponding simulated image of $Ga_2O_3(ZnO)_9$.

should be 1:9. Hence, the atomic ratio of Ga:Zn:O in the unit cell is 2:9:12, which is in agreement with the chemical formula of the compound. Eight formula units of $Ga_2O_3(ZnO)_9$ are contained within one unit cell. Fig. 3(*b*) shows the simulated image based on this model. It was obtained for a specimen thickness of 4 nm and an underfocus value of 50 nm. The calculated image contrast agrees well with the observed contrast, where the positions of the metal atoms are imaged as dark dots. The wedge-shaped image contrast observed in Fig. 2(*a*) corresponds to the (001) plane of the wurtzite-type ZnO structure. There are some specimen edges (indicated by arrows) which are parallel to the wedge-shaped lattice in Fig. 2(*a*). The cleavage of the specimen along these planes is consistent with the fact that in the wurtzite-type ZnO structure the binding between the (001) crystal planes of ZnO is weak.

The existence of a Ga–O layer was confirmed by EDS analysis, shown in Fig. 4, where the electron beam was incident along the [100] orientation of $Ga_2O_3(ZnO)_9$ onto the region to be analyzed. Fig. 4(*a*) is a typical EDS spectrum taken from a large area of about 25 nm. It can be seen that the Ga and Zn peaks located on the high-energy side can be used to monitor the change of the Ga:Zn atomic ratio. Figs. 4(*b*) and (*c*) are spectra from Ga/Zn–O and Ga–O layers, respectively, with the electron beam focused to about 0.5 nm in diameter. It is obvious that the X-ray peak intensity ratio of Ga:Zn in (*c*) (~1.5) is higher than that in (*b*) (~1.0). This direct analysis suggests that the Ga atoms are ordered in the Ga–O layers.

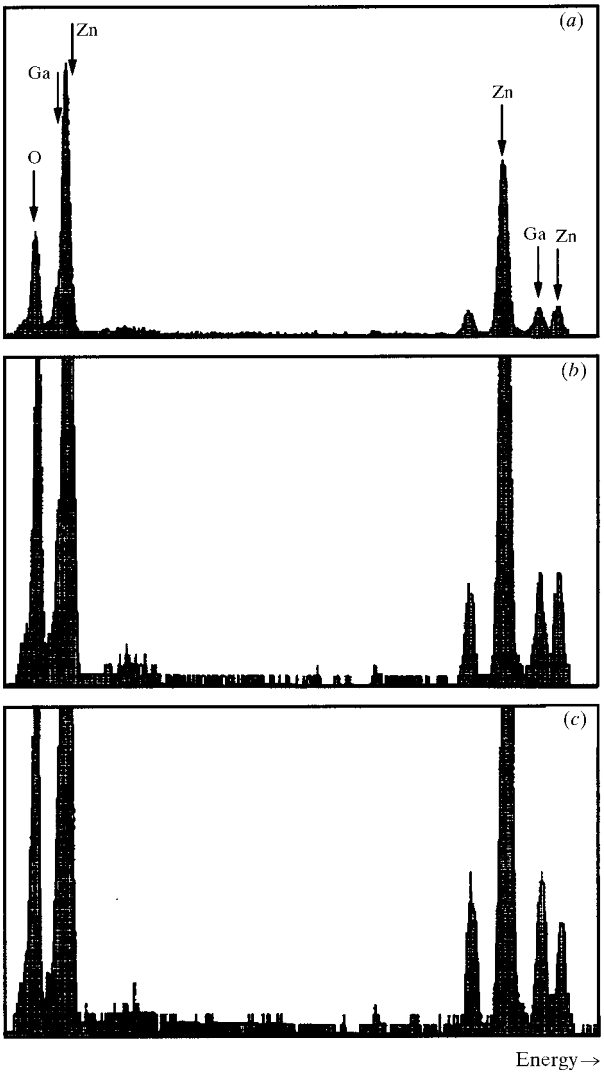

Fig. 4. EDS spectra of $Ga_2O_3(ZnO)_9$. (*a*) was taken from a large area of about 25 nm, showing that the Ga and Zn peaks on the high-energy side are suitable for monitoring the variation of the Ga:Zn atomic ratio. (*b*) and (*c*) are spectra taken from the Ga/Zn–O and Ga–O layers, respectively.

Fig. 5 shows the unit-cell relationship between wurtzite-type ZnO and $Ga_2O_3(ZnO)_9$. The unit-cell base vectors for wurtzite-type ZnO are represented by $\mathbf{a}_{ZnO}$, $\mathbf{b}_{ZnO}$, and $\mathbf{c}_{ZnO}$. $\mathbf{a}_o$ is parallel to $\mathbf{a}_{ZnO}$, and $\mathbf{b}_o$ is parallel to $3\mathbf{OA} - \mathbf{OB} = 3\mathbf{a}_{ZnO}/2 + 3\mathbf{b}_{ZnO} - \mathbf{c}_{ZnO}$. In Fig. 5, we introduce several parameters (**OA**, **OB**, **OC**, **OD**, **CD**, and **OE**) to establish the unit-cell relationship. They are related to the unit cell of ZnO by $\mathbf{OA} = (3)^{1/2}\mathbf{a}_{ZnO}/2$ and $\mathbf{OD} = \mathbf{c}_{ZnO}$. The orthorhombic unit cell can then be expressed in terms of that of ZnO by

$$\mathbf{a}_o = \mathbf{a}_{ZnO}, \tag{1}$$

$$\mathbf{b}_o = 2\mathbf{CD} = 3\mathbf{a}_{ZnO} + 6\mathbf{b}_{ZnO} - \mathbf{c}_{ZnO}, \tag{2}$$

$$\mathbf{c}_o = 24(\mathbf{EO}/3) = 8\mathbf{EO}. \tag{3}$$

Taking $a_{ZnO} = 0.33$ and $c_{ZnO} = 0.52$ nm (Abrahams & Bernstein, 1969), the unit cell of $Ga_2O_3(ZnO)_9$ was

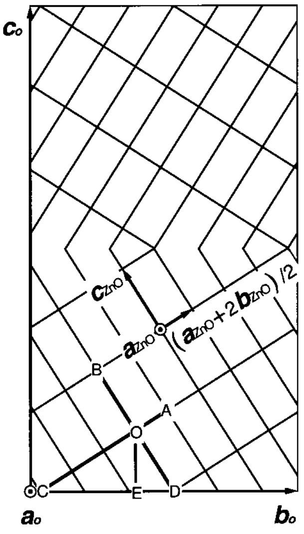

Fig. 5. The unit-cell relation between wurtzite-type ZnO and $Ga_2O_3(ZnO)_9$.

estimated to be $a_o = 0.33$, $b_o = 2.0$, and $c_o = 3.6$ nm, which is in good agreement with the experimental result. We believe that the other $Ga_2O_3(ZnO)_m$ compounds have a similar crystal structure, built up from Ga–O layers interleaved with $m + 1$ Ga/Zn–O layers. The a_o and b_o values of their unit cells can be estimated by (1) and (2), and c_o by $2(m + 3)(EO/3)$.

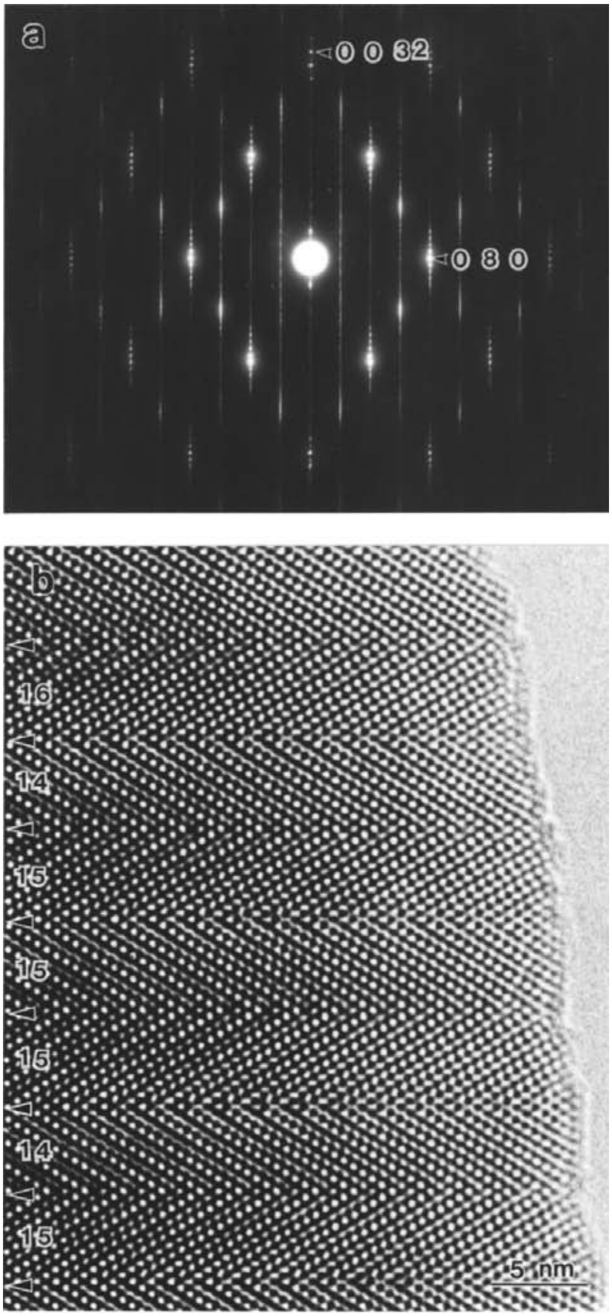

Fig. 6. (*a*) The electron diffraction pattern and (*b*) the corresponding high-resolution image of $Ga_2O_3(ZnO)_{13}$ observed with the incident electron beam parallel to the [100] direction.

To examine the validity of the argument above, Figs. 6(*a*) and (*b*) show the electron diffraction pattern and high-resolution image of $Ga_2O_3(ZnO)_{13}$. The electron diffraction pattern corresponds to the $\mathbf{b}_o^* - \mathbf{c}_o^*$ reciprocal-lattice section and can be indexed by considering an orthorhombic unit cell with $a_o = 0.34$, $b_o = 2.0$, and $c_o = 4.6$ nm. The formula obtained from Fig. 5 predicted a unit cell of $a_o = 0.33$, $b_o = 2.0$, and $c_o = 4.8$ nm for this compound. The measured and predicted lattice constants are consistent with each other.

It should be noted that diffuse streak scattering appeared along the c_o^* axis in the electron diffraction pattern of Fig. 6(*a*). It corresponds to the intergrowth which can be seen in the high-resolution image of Fig. 6(*b*), *i.e.* the number of Ga/Zn–O layers sandwiched by two neighboring Ga–O layers changes from 14 to 16, while this number should be 14 from the chemical formula. It should be mentioned that layers corresponding to smaller m values were also observed; these results are not presented here for brevity. It is the existence of layers with smaller m which causes the measured value of c_o to be smaller than the predicted value in $Ga_2O_3(ZnO)_{13}$. Since there is no obvious diffuse scattering in the diffraction patterns of $Ga_2O_3(ZnO)_9$, we conclude that under the same preparation conditions the crystal quality of compounds with smaller m is better than for those with larger m in the $Ga_2O_3(ZnO)_m$ series. This work was carried out mainly on $Ga_2O_3(ZnO)_9$ rather than on $Ga_2O_3(ZnO)_{13}$ for this reason.

Fig. 7(*a*) is the electron diffraction pattern of $Ga_2O_3(ZnO)_9$ corresponding to the $\mathbf{b}_o^* - \mathbf{c}_o^*$ reciprocal-lattice section. In Fig. 7(*a*), a very large area was included to emphasize the unique intensity distribution of the diffraction spots, *i.e.* the intensities of diffraction spots whose position vectors are an integer combination of $\mathbf{K}_1 = 8\mathbf{b}_o^*$ and $\mathbf{K}_2 = -4\mathbf{b}_o^* + 12\mathbf{c}_o^*$ are higher than the intensities of the surrounding spots. This feature also appeared in the simulated diffraction pattern shown in Fig. 7(*b*), where $\mathbf{K}_1$ and $\mathbf{K}_2$ are indicated. As illustrated in Fig. 3, the structure of the Ga/Zn–O layer is based on the connection of $(Ga/Zn)O_4$ tetrahedra sharing common apices. In the $\mathbf{b}_o - \mathbf{c}_o$ plane, the positions of the atoms of these tetrahedra are related to each other by an average shift of $\mathbf{b}_o/8 + \mathbf{c}_o/24$, examples of which are indicated as **A**–**D** in the structural model in Fig. 3. These atoms contribute to the structure factor of an $0kl$ reciprocal-lattice spot according to $\sum \exp\{2\pi i[(ky + lz + jk/8) + (jl/24)]\}$, where y and z are the coordinates of an A atom in the $\mathbf{b}_o - \mathbf{c}_o$ plane and the summation j should be carried over all the related atoms. This expression reaches a maximum value when $\mathbf{K}$ is an integer combination of $\mathbf{K}_1 = 8\mathbf{b}_o^*$ and $\mathbf{K}_2 = -4\mathbf{b}_o^* + 12\mathbf{c}_o^*$, which is the reason for the unique intensity distribution. A similar result was observed in $Ga_2O_3(ZnO)_{13}$ as well, as seen in Fig. 6(*a*).

It is valuable to compare the crystal structure of $Ga_2O_3(ZnO)_m$ with those of $In_2O_3(ZnO)_m$ and $Fe_2O_3(ZnO)_m$. Representing these compounds by a common chemical formula $M_2O_3(ZnO)_m$, the crystal structure of all of these compounds can be considered as the successive connection of *M*–O and $(m + 1)$ *M*/Zn–O layers. While the *M*/Zn–O layers have similar structures, the structures of the *M*–O layers are different. In $In_2O_3(ZnO)_m$ and $Fe_2O_3(ZnO)_m$, the *M* (*M* = In, Fe) atoms occupy the octahedral sites, while in $Ga_2O_3(ZnO)_m$ the *M* (*M* = Ga) atoms occupy the tetrahedral sites. The typical distance from the center of an octahedron of close-packed O atoms to the nearest O atom is 0.23 nm and the necessary bond lengths for this site to be occupied by In, Fe, and Ga are 0.220, 0.204, and 0.202 nm (Shannon, 1976), respectively. The relatively smaller Ga ionic radius, which probably makes Ga unsuitable for the octahedral sites, provides one possible explanation for the change in structure from those of $In_2O_3(ZnO)_m$ and $Fe_2O_3(ZnO)_m$ to that of $Ga_2O_3(ZnO)_m$.

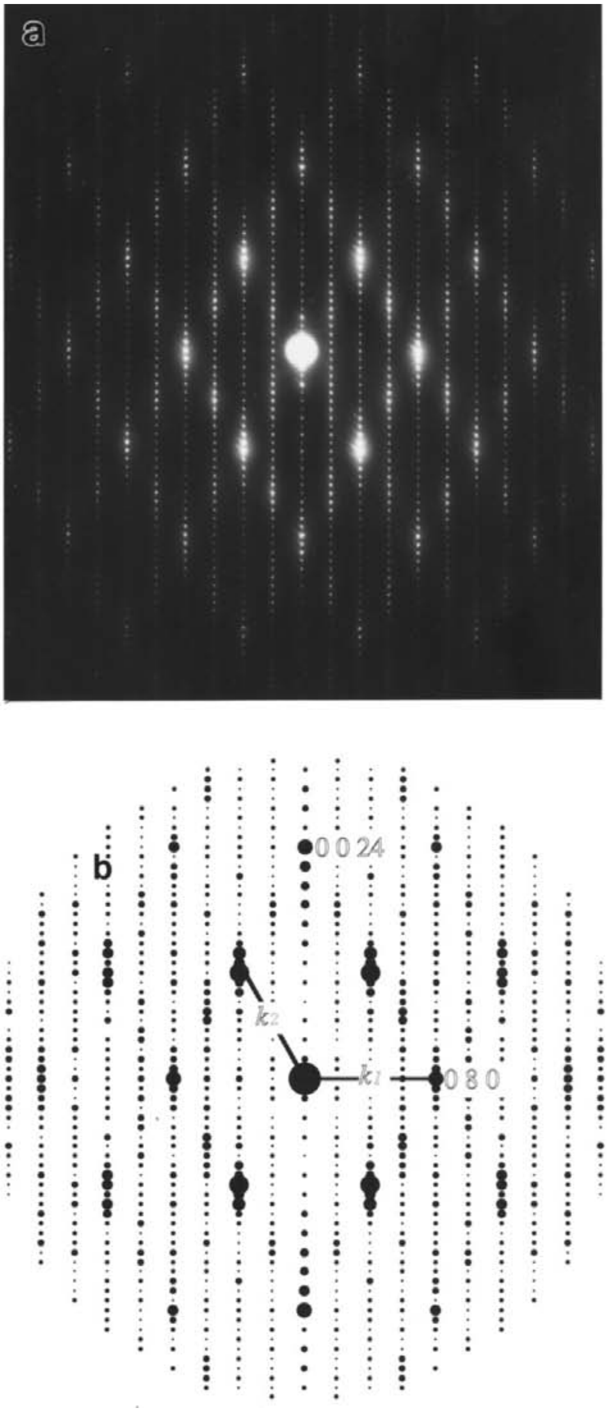

Fig. 7. (*a*) Observed and (*b*) simulated electron diffraction patterns of $Ga_2O_3(ZnO)_9$, corresponding to the $\mathbf{b}_o^* - \mathbf{c}_o^*$ reciprocal-lattice section. The intensities of diffraction spots for which the position vectors are an integer combination of $\mathbf{K}_1$ and $\mathbf{K}_2$ are higher than those of the surrounding spots.

4. Conclusion

The crystal structure of a series of new homologous compounds $Ga_2O_3(ZnO)_m$ (m = 9 and 13) has been studied by high-resolution analytical transmission electron microscopy. It was found that $Ga_2O_3(ZnO)_m$ belongs to the orthorhombic crystal system. From the extinction rules, the possible space groups $Cmc2_1$ (No. 36), $C2cm$ (No. 40), and $Cmcm$ (No. 63) were selected. The unique space group $Cmc2_1$ (No. 36) was then derived from structural requirements. The structure of $Ga_2O_3(ZnO)_m$ can be built from the successive connection of Ga–O and $(m + 1)$ Ga/Zn–O layers, where Ga and Zn atoms occupy the tetrahedral sites formed by the O atoms.

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