Dependence of electrical conductivity of $\beta$-Ga$_2$O$_3$ ceramics on oxygen partial pressure and formation of dislocations

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The electrical conductivity of porous and high-purity $\beta$-Ga$_2$O$_3$ ceramics was measured as a function of oxygen partial pressure, $p_{O_2}$, at 700 to 900 °C. In the high $p_{O_2}$ range, the conductivity was proportional to about $-1/4$th power of $p_{O_2}$, while in the lower $p_{O_2}$ range less than about $10^{-8}$ atm its exponent was $-0.1$ to $-0.13$. This suggests that different types of defects were formed at high and low $p_{O_2}$. The point defect of doubly ionized interstitial gallium ion causes the exponent of $-1/4$, the same value of the experiment in high $p_{O_2}$. When $p_{O_2}$ was changed, the electrical conductivity first changed sharply, followed by a slow change, suggesting some migrations and/or formation of crystalline defects, and so on. In the Ga$_2$O$_3$ samples, many dislocations, with density of about $10^{12}$ cm$^{-2}$, were observed. As the source of carriers, such as dislocations, should be considered as well as point defects.

Key-words : Gallium oxide, Oxide semiconductor, Dislocation, Electrical conductivity, Oxygen partial pressure

1. Introduction

Recently, $\beta$-gallium oxide, $\beta$-Ga$_2$O$_3$, has been attracting much attention as an n-type semiconductor device for power devices and optoelectronic devices for the UV region$^{1,2}$, which is due mainly to its large bandgap of approximately 4.9 eV and its theoretical high breakdown voltage of 8 MV/cm$^{3-5}$ Additionally, it has a congruent melting point and has an advantage over the other nonoxide semiconductor materials used for power devices, such as SiC and GaN, of easily being fabricated into a single crystal$^{6,7}$ Optoelectronic applications in the UV region are often examined by using thin films that are fabricated by a sol–gel method$^{8,9}$, PLD$^{10}$, simple evaporation of the gallium source$^{11,12}$ and sputtering$^{13,14}$

The crystal structure of $\beta$-Ga$_2$O$_3$ was reported as a monoclinic crystal system with $a = 12.214$, $b = 3.0371$, $c = 5.7981$ Å, and $\beta = 103.83^\circ$.$^{15}$ In the structure, the gallium ions occupy the tetragonal and octahedral polyhedra formed by oxide ions. The octahedra are linked by sharing an edge along the $b$-axis and the tetrahedra combine them through an apex sharing.

Because the electrical properties of oxide semiconductors are greatly influenced by the nonstoichiometry of the compounds, the chemical defects of $\beta$-Ga$_2$O$_3$ have been extensively studied. Recently, Johnson et al. investigated $\beta$-Ga$_2$O$_3$ by STEM images and DFT simulation.$^{16}$ They concluded that a defect complex of two gallium ion vacancies with a single interstitial gallium ion [$2V_{Ga}\text{-Ga}^\text{i}$] is formed. In this case, the composition of the compound became gallium ion deficient, although they did not mention the defect charge. Because $\beta$-Ga$_2$O$_3$ is n-type oxide semiconductor, the composition should be either oxide ion deficient or metal ion excessive. Therefore, the formation of the additional defect other than the defect complex of [$2V_{Ga}\text{-Ga}^\text{i}$] should also be considered. Regarding the formation of an oxide ion vacancy, the formation energy of the neutral and doubly ionized vacancies was calculated to be a deep state.$^{17}$ The deep donor level of the oxide ion vacancy was also calculated by Varley et al.$^{18}$ who stated that the oxide ion vacancy cannot be a source of the intrinsic conductivity.

Several other experimental studies on the defect levels have been reported that do not specify the type of defect. Three defect levels were commonly identified at approximately 1.0, 0.8, and 0.6 eV below the edge of the conduction band.$^{19,20}$ Additionally, a rather shallow defect level of approximately 0.13 eV was reported.$^{21,22}$ This level may cause the unintentional conductivity. These studies postulate the static existence of the defects. However, the defect and its density in a nonstoichiometric oxide semiconductor depends on the ambient $p_{O_2}$ and the temperature.

A traditional experiment to study the defect formation in nonstoichiometric oxide compounds is to measure the electrical conductivity when the oxygen partial pressure is varied at high temperatures.$^{23,24}$ The exponent of the dependence of conductivity on $p_{O_2}$ indicates that the defect formed in the semiconductor, and this measurement can be in situ.
In 1974, Sasaki et al.\textsuperscript{25} reported the dependence of the conductivity of a $\beta$-Ga$_2$O$_3$-sintered sample on the oxygen partial pressure, $p_{O_2}$, at 800 to 950°C and within a $p_{O_2}$ range from $4 \times 10^{-5}$ to 1 atm. They concluded that there were two different dependences on $p_{O_2}$, and in a high $p_{O_2}$ region, the conductivity was proportional to $p_{O_2}^{-1/4}$. Additionally, they deduced the formation of a singly ionized oxide ion vacancy or a doubly ionized interstitial gallium ion. In a $p_{O_2}$ range lower than $8 \times 10^{-4}$ atm, their measurements had no $p_{O_2}$ dependence. The same result, i.e., that conductivity is proportional to $p_{O_2}^{-1/4}$, has been reported for $\beta$-Ga$_2$O$_3$ films made by sputtering and screen printing.\textsuperscript{13,26} These studies clearly demonstrate that conductivity is proportional to $p_{O_2}^{-1/4}$; however, the dependence under a lower $p_{O_2}$ has not yet been clarified.

Here, we report the results of the measurements of the $p_{O_2}$ dependence of the electrical conductivity of a porous $\beta$-Ga$_2$O$_3$ polycrystal. The dependence was not constant and changed at some $p_{O_2}$. The conductivity of the $\beta$-Ga$_2$O$_3$ ceramic continued to change over time under specific conditions. In the samples that were reduced for a long time at 800°C, dislocation with an extremely high density was observed by transmission electron microscope (TEM).

2. Experimental procedures

A $\beta$-Ga$_2$O$_3$ ceramic was fabricated using high purity powder (99.999 % pure, NewMet Koch). After the powder was isostatic pressed into a disc with a 20 mm diameter and a thickness of approximately 2.5 mm at 100 MPa, it was heated at 1500°C for 2 h. The sample was cut to a rectangular bar and platinum wires were set with flint-less porous platinum paste; then, it was baked at 1200°C. The sample was set in a furnace, in which $p_{O_2}$ was controllable. The in situ conductivity of the $\beta$-Ga$_2$O$_3$ ceramic was measured using the two-terminal DC method at 700 to 900°C.

The detailed experimental set up for measuring the conductivity with varying $p_{O_2}$ values was described in our earlier paper.\textsuperscript{27} In short, the oxygen partial pressure was controlled by a simple mixture of N$_2$ and O$_2$ for a high $p_{O_2}$ value ($1 \times 10^{-4}$ atm). The lower $p_{O_2}$ atmosphere was controlled using an oxygen pump operated at 800°C, which was made of a stabilized zirconia tube flowing CO$_2$ and dry/wet N$_2$ for the medium and low $p_{O_2}$, respectively. The $p_{O_2}$ value near the sample was also monitored using a stabilized zirconia oxygen sensor, and this value was used as the atmosphere of the sample. The sample was characterized by an X-ray diffractometer (XRD, Ultima IV, Rigaku, Japan), a scanning electron microscope (SEM, S-4800, Hitachi, Japan), and a TEM (JEM-2100, JEOL, Japan).

3. Results and discussion

3.1 Sintered sample and electrical conductivity

Figure 1 showed TEM micrographs of the powder. The powder consists of cylindrical and fine granular particles. The cylinder-shaped particle comprises many fine particles, indicating that they are obtained by pyrolysis of gallium salts or hydroxides.

![Fig. 1. Transmission electron micrographs of as-received Ga$_2$O$_3$ powder.](image)

The resultant ceramic after firing at 1500°C was porous, and its density was approximately 65% of the theoretical density of 5.95 g/cm$^3$. The SEM micrograph is shown in Fig. 2. A porous structure was observed, with a grain size ranging from 3 to 10 µm and where some of the grains were rectangular in shape. Due to the high porosity, the reaction with the gas would occur quickly. The resultant sample is confirmed to be $\beta$-Ga$_2$O$_3$ by XRD.

Examples of change in the measured electrical conductivity, $\sigma$, of the $\beta$-Ga$_2$O$_3$ bar against time, $t$, are shown in Figs. 3 and 4. As the $p_{O_2}$ decreased, the conductivity of the sample increased. This is typical for the n-type oxide semiconductors. If the carrier concentration is determined by the impurities, the electrical conductivity should be almost constant. However, as shown in Figs. 3 and 4, the conductivity changes with oxygen partial pressure. This means that the carrier concentration is not determined by the impurities. There seem to be two types of conductivity changes, i.e., the instantaneous changes when $p_{O_2}$ is changed and the slow changes that follow. The two types of change were in the same direction. When $p_{O_2}$ decreased, the instantaneous change and subsequence gradual changes were toward increasing conductivity and vise-versa. At 800°C, as shown in Fig. 3, the conductivity values under the same $p_{O_2}$ were the same. This means that the gradual change is not a destructive change. On the other hand, at 900°C as shown in Fig. 4, the conductivity values under...
the same \( p_{O_2} \) were not the same; for the value when decreasing and then increasing the \( p_{O_2} \), see the value of \( p_{O_2} = 10^{1.5} \) atm indicated by the two arrows in Fig. 4. When the sample was under the lower \( p_{O_2} \) at 900 °C and then returned to \( p_{O_2} = 10^{1.5} \) atm, the conductivity decreased from 8.1 \( \times 10^{-4} \) to 6.1 \( \times 10^{-4} \) S/cm. The initial value seemed to be saturated, but the second time it continued to fall. It is known that \( \beta\text{-Ga}_2\text{O}_3 \) tends to decompose into volatile \( \text{GaO} \), \( \text{Ga}_2\text{O} \) and \( \text{Ga} \) species and oxygen at a high temperature and low \( p_{O_2} \).\(^6\) The distractive decomposition of \( \beta\text{-Ga}_2\text{O}_3 \) causes a decrease in the contact area between the \( \beta\text{-Ga}_2\text{O}_3 \) grains and between the platinum electrodes and \( \beta\text{-Ga}_2\text{O}_3 \) grains, which led to the decreasing conductivity at the same \( p_{O_2} \) with time. Therefore, the conductivity \( \sigma \) measured at 700 and 800 °C were plotted against the \( p_{O_2} \) values in Fig. 5. During the experiment, an abrupt decrease in conductivity, which was reported for the thin films,\(^28\) did not occur.

Since the conductivity changed during soaking at a constant \( p_{O_2} \), the data was obtained after a rather long duration of approximately 8 to 12 h. The experimental data was obtained in the decreasing and increasing \( p_{O_2} \) periods, and the change in \( p_{O_2} \) was repeated several times. Figure 5 shows the conductivity of the sample at various \( p_{O_2} \) values. It is obvious that there are two different slopes, which change at a \( p_{O_2} \) value of approximately \( 10^{-5} \) atm. The tendency was the same at 700 and 800 °C. This means that there are at least two types of defects and the dominant defect change occurs at \( p_{O_2} = 10^{-5} \) atm. Assuming that the different types of defects corresponding to the two slopes coexist and that the defect concentration, i.e., the carrier concentration, varies with \( p_{O_2} \), the electrical conductivity can be considered to change as shown by the dashed lines extrapolated from the measured values at 800 °C in Fig. 5. The measured data in Fig. 5 do not show the coexistence of the two types of defects, and the defect type altered at \( p_{O_2} = 10^{-5} \) atm.

The slope of approximately \(-0.21 \text{ to } -0.22\) was almost the same as that of the previous paper, i.e., \(-1/4\). However, the slope was not derived from the simple consideration of the defect; the doubly ionized oxide ion vacancy, \( V_{O}^{2+} \), and the triply ionized interstitial gallium ion, \( \text{Ga}^{3+} \), has the slopes of \(-1/6\) and \(-3/16\), respectively.

The exponent of approximately \(-1/4\) was considered by Sasaki,\(^25\) who proposed two defect types. If we consider doubly ionized interstitial gallium ion, the next equilibrium equation can be drawn:

\[
\text{Ga}_2\text{O}_3 \rightleftharpoons \text{Ga}_{2+} + 1.5\text{O}^- + \text{Ga}^{3+} + \frac{3}{4}\text{O}_2 + 2\text{e}^-.
\]  (1)

An electrically neutral condition is \( 2[\text{Ga}^{3+}] = [\text{e}^-] = n \). Here \( n \) is carrier concentration. Therefore, the equilibrium constant is as follows:

\[
K = \frac{[\text{Ga}_{2+}][\text{O}_2]^{1.5}[\text{Ga}^{3+}][\text{e}^-]^{3/4}}{[\text{Ga}_2\text{O}_3]}.
\]  (2)
The values of \([\text{Ga}_2\text{O}_3]\), \([\text{Ga}^{3+}_d]\), and \([\text{O}_2^-]\) can be considered as unity,

\[
\text{then } K = \frac{1}{2} P_{02}^{1/4} n^3 \text{ and } n \propto P_{02}^{-1/4}.
\]

The doubly ionized interstitial gallium ion means that an electron is trapped at the interstitial \(\text{Ga}^{3+}\) ion. Another possibility is a singly ionized oxide ion vacancy, as follows:

\[
\text{Ga}_2\text{O}_3 \rightleftharpoons 2\text{Ga}^{3+}_d + 2\text{O}^2_2^- + \text{V}^+_o + \frac{1}{2} \text{O}_2^0 + e^-.
\]

An electrically neutral condition is \([V^+_o] = n\) and \(K = P_{02}^{1/2} n^5\). Therefore, \(n \propto P_{02}^{-1/4}\) is derived. In both cases, the slope is \(-0.25\) and close to the experimental result. The formation of oxide ion vacancy, however, does not seem to cause the decrease of the conductivity, because the formation of the oxide ion vacancy is calculated to be difficult.\(^{17,18}\)

Instead, \(\text{Ga}^{3+}_d\) may be formed.

The smaller slope in lower \(P_{02}\) range could not be explained yet. If we consider the singly ionized interstitial gallium ion, \(\text{Ga}^{3+}_d\), the \(P_{02}\) dependence with an exponent of \(-3/8 = -0.375\) results, which suggests the formation of some defect complex, as Johnson et al. reported\(^{10}\) and/or the other defects may generate the carriers.

### 3.2 Slow change in conductivity and oxygen diffusion model

As shown in Figs. 3 and 4, the slow change in the conductivity after the prompt change at the constant \(P_{02}\) seems to cause some phenomena that is controlled by diffusion. A simple consideration is that a surface reaction with an ambient atmosphere occurs and the gradual increase of the thickness of the surface layer causes the long-time change in the conductivity. To examine the change, the electrical resistance of a hemisphere with a surface layer of different resistivity was calculated, as shown in Fig. 6(a).

The hemisphere radius was set to one and the surface layer thickness, \(\Delta r\), was considered. The high and low resistivities were 10 and 1, respectively. The value ratio corresponded to the conductivity change shown in the different resistance surface layer and inside, the thickness of the surface layer, \(\Delta r\), increases with time.

Fig. 3(b). The resistances of the surface ring and inside disc were calculated and added. The resistance was calculated from \(x = 0\) to 0.866, at which the radius of the cut circle becomes 0.5. In addition to the surface layer, an interface layer of a half thickness having the same resistivity with the surface layer was considered as a grain boundary layer. The thickness of the surface layer, \(\Delta r\), can be considered to increase in proportion to the root-square of time, assuming a usual diffusion-controlled reaction. The calculation was conducted until \(\Delta r = 0.95\). The resistance changes corresponding to the changes of decreasing and increasing \(P_{02}\) were calculated. The calculations correspond to the low and high resistance surface layers. The two calculations indicate the change in conductivity when \(P_{02}\) changes to a higher or a lower value when the atmosphere is changed during the experiment. The resultant changes are shown in Fig. 6(b).

Although an initial change in the conductivity is rapid and a slow change follows in both cases, it is only after the value is about halfway through that a sudden change turns into a slow change. This is especially noticeable when the conductivity is reduced. This suggests that the change in the conductivity shown in, for example, Fig. 3 was not the change by the change in the surface layer thickness of a different conductivity. This mean that after changing the \(P_{02}\), formation of point defects completed, a different type of structure change followed. The following change in the structure may be, for instance, a clustering of the point defects. When the \(P_{02}\) value is reduced, the number of defects increase, which implies an increase in the enthalpy of the defect formation. To reduce the enthalpy, defect clustering, for example, may occur. Usually, the entropy term is emphasized in the consideration of the defect formation, but in the present isothermal conditions, the enthalpy term has a significant influence. The clustering of defects reduces the number of defects and, consequently, reduces the scattering center of the electron transport. In other words, when the \(P_{02}\) value decreased, the instantaneous change in conductivity was due to the increasing carrier concentration, and the following slow change was...
due to the increase in mobility, although it is only speculation now.

### 3.3 TEM observation and formation of dislocations

The as-received powder was observed by TEM. Additionally, $\beta$-$\text{Ga}_2\text{O}_3$ ceramics were heated at 800 °C for 336 h in $p_{\text{O}_2} = 10^{-16}$ atm and for 100 h in air. After being crushed in a mortar, they were also observed by TEM. Figure 7 shows typical images of samples of the as-received and heated in $p_{\text{O}_2} = 10^{-16}$ atm. The images were taken from the $c$-axis direction of $\beta$-$\text{Ga}_2\text{O}_3$. Unit cell axes are also shown. The $a$-axis is inclined in a downward direction by an angle $\beta$, 103.83°. As is clearly shown inside the circle in Fig. 7(b), a typical edge dislocation was observed. The Burgers vector of the dislocation has a component along the $a$-axis. A quarter plane of (100) is deleted, which will be presented in a later section.

The $\beta$-$\text{Ga}_2\text{O}_3$ ceramic heated at 800 °C for 100 h in air was observed by TEM, and an image is shown in Fig. 8. The image was also taken from the $c$-axis direction. In this observation, the lattice image near the center is tilted, which suggests the existence of a screw dislocation. The screw dislocation lies perpendicular to the $c$-axis, and the Burgers vector has a component along $a$-axis.

Another image of the $\beta$-$\text{Ga}_2\text{O}_3$ ceramic heated in $p_{\text{O}_2} = 10^{-16}$ atm for 336 h at 800 °C is shown in Fig. 9. At least six edge dislocations were observed in the shown area of 17.2 nm x 16.3 nm. The density of the dislocation in the image was calculated as approximately $2 \times 10^{12}$/cm², which is almost the same value as a severely work hardened metal. The dislocation density of the $\beta$-$\text{Ga}_2\text{O}_3$ single crystal was reported as being approximately $10^5$/cm² by means of the etch pit density and $5 \times 10^3$/cm² by means of a laser scattering tomography. The present sample had a much larger number of dislocations.

It is interesting that the dislocations with opposite signs were neighboring, as shown in Fig. 9. The stresses caused by these dislocations are locally cancelled. This arrangement is not the result of applying external stress nor of...
thermal stressed due to thermal contraction anisotropy. The low dislocation density measured by the etch-pit method seem to contradict the present results. This is because the dislocations in the locally stress-cancelled area did not appear through the etching. Another possible explanation for this difference in density is that our sample is a sintered ceramic of $\beta$-Ga$_2$O$_3$ powder initially having dislocations, while theirs is a single crystal. As shown in Fig. 7(a), it is thought that dislocations existed in the raw powder used, which remained after sintering and subsequent grain growth.

The schematics of the crystal structure viewed from [010] and [001] directions are shown in Figs. 10(a) and 10(b), respectively. The $a$-axis is inclined in a downward direction in Fig. 10(b). The gallium ions as well as the polyhedra are arranged along the $b$-axis. The hatched area corresponds to a quarter semiplane of (100) parallel to the $b$-axis and $c$-axis, and this semiplane is removed to form an edge dislocation. It is noteworthy that the plain does not have translation symmetry with the adjacent planes. Once a dislocation is introduced, it is difficult to eliminate by a glide and/or climb of the dislocations, which is the reason for the coexistence of dislocations with opposite signs occurring in proximity and remaining after sintering and grain growth.

So far, the mechanism of carrier generation in non-stoichiometric oxide semiconductors has been assumed to be due to the formation of point defects such as vacancies and interstitial ions, as shown in Eqs. (1) and (4). However, under conditions where many dislocations are generated, it is necessary to consider line defects such as dislocations as a carrier generation mechanism as well. If one carrier generation occurs per $5\,\AA$ of dislocation, then dislocation with a density of $10^{12}/\text{cm}^2$ would generate $2 \times 10^{19}/\text{cm}^3$ carriers. The concentration is a significant amount and affects the electrical conductivity of the semiconductor as a major factor.

Unfortunately, it is not yet clear whether the formation of dislocations is related to the gradual change in the conductivity in Figs. 3 and 4, and the change in the slopes in Fig. 5. However, as a source of carriers, it is necessary to consider not only the point defects and their complex but also the line defects, such as dislocations.

4. Conclusions

We demonstrated the dependences of conductivity on the $p_{O_2}$ values of high purity $\beta$-Ga$_2$O$_3$ ceramics, and two dependences at low and high $p_{O_2}$ ranges were obtained. This suggests the formation of two types of different chemical defects. In a $p_{O_2}$ range higher than approximately $10^{-5}\text{ atm}$, the conductivity was proportional to $-1/4$ power of $p_{O_2}$ and this value is deduced by considering the doubly ionized gallium ion interstitial. At the lower $p_{O_2}$ range, the value was less than $-1/4$. The change in the conductivity consisted of an initial prompt change followed by a slow change when the $p_{O_2}$ was changed. Some migration of the formed defects would cause the second slow change. After a long duration at a low $p_{O_2}$ value at 800 °C, many dislocations formed in the sample. As the source of the carrier, the point defects and also the line defects, such as dislocations, should be taken into account.

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References
1) M. Higashiwaki, K. Sasaki, H. Murakami, Y. Kumagai, A. Koukitu, A. Kuramata, T. Masui and S. Yamakoshi, *Semicond. Sci. Tech.*, **31**, 034001 (2016).
2) S. J. Pearton, J. Yang, P. H. Cary, F. Ren, J. Kim, M. J. Tadjer and M. A. Mastro, *Appl. Phys. Rev.*, **5**, 011301 (2018).
3) M. Passlack, E. F. Schubert, W. S. Hobson, M. Hong, N. Moriya, S. N. G. Chu, K. Konstadinidis, J. P. Mannaerts, M. L. Schnoes and G. J. Zydzik, *J. Appl. Phys.*, **77**, 686–693 (1995).
4) M. Orita, H. Ohta, M. Hirano and H. Hosono, *Appl. Phys. Lett.*, **77**, 4166–4168 (2000).
5) M. Rebien, W. Henrion, M. Hong, J. P. Mannaerts and M. Fleischer, *Appl. Phys. Lett.*, **81**, 250–252 (2002).
6) Z. Galazka, R. Uecker, K. Irmscher, M. Fleischer, R. Uecker and R. Fornari, *Cryst. Res. Technol.*, **45**, 1229–1236 (2010).
7) H. Aida, K. Nishiguchi, H. Takeda, N. Aota, K. Sunakawa and Y. Yaguchi, *Jpn. J. Appl. Phys.*, **47**, 8506–8509 (2008).
8) Y. Kokubun, K. Miura, F. Endo and S. Nakagomi, *Appl. Phys. Lett.*, **90**, 031912 (2007).
9) Y. Ohya, J. Okano, Y. Kasuya and T. Ban, *J. Ceram. Soc. Jpn.*, **117**, 973–977 (2009).
10) S. Müller, H. von Wenckstern, D. Splith, F. Schmidt and M. Grundmann, *Adv. Phys. A*, **211**, 34–39 (2014).
11) T. Oshima, T. Okuno, N. Arai, N. Suzuki, S. Ohira and S. Fujita, *Appl. Phys. Express*, **1**, 011202 (2008).
12) S. Nakagomi, T. Momoi, S. Takahashi and Y. Kokubun, *Appl. Phys. Lett.*, **103**, 072105 (2013).
13) M. Fleischer and H. Meixner, *Sensor. Actuat. B-Chem.*, **4**, 437–441 (1991).
14) T. Miyata, T. Nakatani and T. Minami, *Thin Solid Films*, **373**, 145–149 (2000).
15) J. Ahman, G. Svensson and J. Albertsson, *Acta Crystallogr. C*, **52**, 1336–1338 (1996).
16) J. M. Johnson, Z. Chen, J. B. Varley, C. M. Jackson, E. Farzana, Z. Zhang, A. R. Arehart, H.-L. Huang, A. Genc, S. A. Ringel, C. G. Van de Walle, D. A. Muller and J. Hwang, *Phys. Rev. X*, **9**, 041027 (2019).
17) Z. Hajnal, J. Miro, G. Kiss, F. Reti, P. Deak, R. C. Hemond and J. M. Kuperberg, *J. Appl. Phys.*, **86**, 3792–3796 (1999).
18) J. B. Varley, J. R. Weber, A. Janotti and C. G. Van de Walle, *Appl. Phys. Lett.*, **97**, 142106 (2010).
19) K. Irmischer, Z. Galazka, M. Pietsch, R. Uecker and R. Fornari, *J. Appl. Phys.*, **110**, 063720 (2011).
20) Z. Zhang, E. Farzana, A. R. Arehart and S. A. Ringel, *Appl. Phys. Lett.*, **108**, 052105 (2016).
21) A. T. Neal, S. Mou, R. Lopez, J. V. Li, D. B. Thomson, K. D. Chabak and G. H. Jessen, *Sci. Rep.*, **7**, 13218 (2017).
22) S.-S. Huang, R. Lopez, S. Paul, A. T. Neal, S. Mou, M. Houng and J. V. Li, *Jpn. J. Appl. Phys.*, **57**, 091101 (2018).
23) P. Kofstad, "Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides", Wiley Inter-science, Wiley & Sons, New York (1972) Chaps. 2–4.
24) O. T. Soresens, "Nonstoichimetric Oxides", Academic Press, New York (1981) Chaps. 5–6.
25) T. Sasaki and K. Hijikata: Proc. Inst. Nat. Sci. Nihon Univ. No. 9 (1974) pp. 29–35.
26) A. Feltz and E. Gansjager, *J. Eur. Ceram. Soc.*, **18**, 2217–2226 (1998).
27) Y. Ohya, T. Yamamoto and T. Ban, *J. Am. Ceram. Soc.*, **91**, 240–245 (2008).
28) M. Fleischer, L. Höllbauer, E. Born and H. Meixner, *J. Am. Ceram. Soc.*, **80**, 2121–2125 (1997).
29) S. Banerjee, J. K. Chakravarty, J. B. Singh and R. Kapoor, “Functional Materials”, Elsevier (2012) Chap. 11.
30) Z. Galazka, K. Irmischer, R. Uecker, R. Bertram, M. Pietsch, A. Kwasiwserski, M. Naumann, T. Schulz, R. Schewski, D. Klimm and M. Bickermann, *J. Cryst. Growth*, **404**, 184–191 (2014).