Construction of Structural Phase Diagram of LaGa$_{1-x}$Mg$_x$O$_{3.8}$ by Using Various Diffraction Measurements and Thermal Analyses
-Effect of Long Period Anti-Phase Domain Structure on Phase Diagram-

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Construction of structural phase diagram of LaGa$_{1-x}$Mg$_x$O$_{3.8}$ has been attempted by using synchrotron X-ray diffraction, high temperature X-ray diffraction, dilatometry and differential scanning calorimetry. Existence of long-period anti-phase domain structure(LPAPDS) observed in the specimens with $x$ larger than 0.10 by using electron diffraction analysis was considered for the phase diagram construction. Existence of four phases has been proposed and their phase relationship has been evaluated. For the specimen with $x = 0.00$, orthorhombic phase free from LPAPDS and rhombohedral phase without LPAPDS were detected. In LaGa$_{1-x}$Mg$_x$O$_{3.8}$ with $x$ larger than 0.10, orthorhombic phase and rhombohedral phase with LPAPDS were proposed. It was suggested that the slow kinetics of the phase transition from orthorhombic phase with LPAPDS to rhombohedral with LPAPDS was the origin of region, where mixture of orthorhombic phase and rhombohedral phase was observed. Existence of two-phase region, where phase free from LPAPDS and one with LPAPDS coexist, has been clarified. The compositional region, where $x$ is around 0.05, is revealed to be the two-phase region from room temperature to 800°C.

**Key Words**: LaGa$_{1-x}$Mg$_x$O$_{3.8}$ Phase Diagram, Crystal Structure, Thermal Analyses

1 Introduction

In order to decrease the operating temperature of solid oxide fuel cells, alternative electrolyte materials for yttria stabilized zirconia have been desired. Sr$^{2+}$- and Mg$^{2+}$-substituted LaGaO$_3$ is one of the candidate materials, since it shows high oxide ion conductivity at temperatures as low as 600-800°C. The consensus seems to be established that oxide ion vacancies generate by substitution of Sr$^{2+}$ for La$^{3+}$ and Mg$^{2+}$ for Ga$^{3+}$ site, resulting in increase of oxide ion conductivity in LaGaO$_3$ system. It has also been reported that substitution of Sr$^{2+}$ and/or Mg$^{2+}$ affects crystal structure and structural phase transition behavior of LaGaO$_3$ system. The information of crystal structure and phase transition is important from a viewpoint of mechanical stability for practical application. In addition, behavior of oxide ion vacancy affecting oxide ion conductivity, such as clustering, might be deduced from crystal structure. However, there exists contradiction in literatures even on crystal structure of simple substitution system, LaGa$_{1-x}$Mg$_x$O$_{3.8}$.

Martí and coworkers reported that the crystal structure of LaGaO$_3$ is an orthorhombic distorted perovskite structure with space group of $Pbnm$ (No. 62) and lattice constants of $\sqrt{2} a_0 \times \sqrt{2} a_0 \times 2 a_0$, where $a_0$ is a lattice constant of pseudocubic perovskite structure, from neutron diffraction measurements. They also found the first order structural phase transition from orthorhombic to rhombohedral phase at about 150°C, which was also confirmed with thermal analyses by other researchers.

Slater et al. and Lerch et al. measured powder neutron diffraction of LaGaO$_3$ at various temperatures. Slater et al. reported that the space group of LaGaO$_3$ was $Pbnm$ (No. 62) at room temperature and $R3c$ (No. 161) above 250°C. The conclusion of Lerch and coworkers on crystal structure at room temperature agreed with those of Slater and coworkers, however, they proposed the space group of high temperature phase was $R3c$ (No. 167). Kajitani and coworkers reported that crystal structure of LaGaO$_3$ is orthorhombic distorted perovskite with space group of $Pbnm$ (No. 62) from Rietveld analysis of neutron diffraction patterns. They also reported high temperature X-ray diffraction measurement of LaGa$_{0.8}$Mg$_{0.2}$O$_{3.5}$, indicating that its crystal system changed to rhombohedral at 800°C. One of the authors (T. Hashimoto) performed synchrotron or high temperature X-ray diffraction on single phase LaGaO$_3$, LaGa$_{0.8}$Mg$_{0.2}$O$_{3.25}$ and LaGa$_{0.8}$Mg$_{0.2}$O$_{3.2}$ and proposed that space group of LaGa$_{0.8}$Mg$_{0.2}$O$_{3.25}$ and LaGa$_{0.8}$Mg$_{0.2}$O$_{3.2}$ at room temperature was $Ibmm$ (No. 74) from extinction rule. In this report, the crystal structure of LaGa$_{0.8}$Mg$_{0.2}$O$_{3.25}$ and LaGa$_{0.8}$Mg$_{0.2}$O$_{3.2}$ change to rhombohedral with space group of $R3c$ (No. 167) above 600°C and 750°C, respectively. Kajitani et al. reexamined their neutron diffraction patterns of LaGa$_{0.8}$Mg$_{0.2}$O$_{3.2}$ system and obtained consistent results with ones reported in ref. (10).

In order to settle above contradiction, we have tried to determine space group of LaGa$_{1-x}$Mg$_x$O$_{3.8}$ experimentally...
by selected area and convergent beam electron diffraction.\textsuperscript{12} It was clarified that the space group of both \( \text{LaGa}_2 \) and \( \text{LaGa}_{14}\text{MgO}_{3.8} \) was \( \text{Pbnm} \) (No. 62) and that the diffraction intensity of \( h + k + l = \text{odd} \) signal in \( \text{LaGa}_{14}\text{MgO}_{3.8} \) was so low that the powder diffraction pattern can also be explained as false space group, \( \text{Pbnm} \) (No. 74).\textsuperscript{10,11} In \( \text{LaGa}_{14}\text{MgO}_{3.8} \), existence of long-period anti-phase domain structure (LPAPDS) was also indicated from splitting of electron diffraction spots, whereas the splitting was not observed in electron diffraction in \( \text{LaGa}_2 \). We suppose that the origin of LPAPDS is localization of oxide ion vacancy in the domain due to strong association of \( \text{V}_0 \) and \( \text{Mg}^{2+} \) as predicted by theoretical calculations.\textsuperscript{16,18} Since large activation energy and relatively low oxide ion conductivity has been reported in \( \text{LaGa}_{14}\text{MgO}_{3.8} \) in which LPAPDS should exist, we consider that generation of LPAPDS should be prevented to increase oxide ion conductivity. Therefore, LPAPDS stable regions on Mg content and/or temperatures should be clarified as a first step to control the LPAPDS.

In this study, construction of structural phase diagram of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) considering LPAPDS has been attempted. The crystal structure and phase transition behavior of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) with \( x = 0.00, 0.05, 0.10, 0.15 \) and 0.20 were analyzed by using synchrotron X-ray diffraction, high temperature X-ray diffraction, dilatometry and differential scanning calorimetry (DSC).

## 2 Experimental

\( \text{LaGa}_{14}\text{MgO}_{3.8} \) (\( x = 0.00, 0.05, 0.10, 0.15, 0.20 \)) was prepared by solid state reaction method. \( \text{La}_2\text{O}_3 \) (99.9\%), \( \text{Furuuchi Chemistry Corp.} \), \( \text{Ga}_2\text{O}_3 \) (99.9\%), \( \text{Furuuchi Chemistry Corp.} \), \( \text{MgO} \) (99.9\%, \( \text{Furuuchi Chemistry Corp.} \) were used as starting materials. Before weighing, all the powders were heated at 1000°C more than 12 h in air to decompose impurities such as carbonates and/or hydroxide. Nominal amount of \( \text{La}_2\text{O}_3 \), \( \text{Ga}_2\text{O}_3 \), \( \text{MgO} \) were mixed in ethanol with alumina mortar. The obtained powders were heated at 1100°C for 10 h in a air. The heated powders were grounded in an alumina mortar with a pestle and pressed uniaxially at 30 MPa. The pressed specimens were sintered at 1500°C for 10 h in air, followed by pulverizing and remixing in ethanol. The remixed powders were also pressed uniaxially at 30 MPa and sintered at 1500°C for 10 h in air.

The powder specimen for various measurements were prepared by crushing the sintered bodies. Each specimen was subjected to X-ray diffraction at room temperature (RT-XRD) for confirmation of obtained phase. The temperature dependence of crystal structure in air was examined by X-ray diffraction at high temperatures (HT-XRD). Both measurements were carried out by using RINT-2500VPC (CuK\( \alpha \); 50 kV, 250 mA, Rigaku Co., Ltd.). In order to examine exact crystal system, synchrotron X-ray diffraction measurements at room temperatures were carried out by using BL-4B2 beam line at photon factory, KEK.\textsuperscript{19} The wavelength of synchrotron X-ray was 1.20832 Å.

The phase transition behavior of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) was analyzed with dilatometry and DSC. Dilatometry from room temperature to 900°C was carried out in air with heating and cooling rate of 10°C/min by using TMAB310 (Rigaku Co., Ltd.). Cylindrical sintered specimens with about 5.0 mm diameter and 15-20 mm height were used for the measurements. \( \text{SiO}_2 \) rod was employed as a reference. DSC of powder specimen in temperature range from room temperature to 750°C was performed in air or \( \text{N}_2 \) with heating and cooling rate of 10°C/min by using DSC8230 (Rigaku Co., Ltd.). \( \text{Al}_2\text{O}_3 \) and Pt were used as a reference and pan, respectively.

## 3 Results and Discussion

### 3.1 Crystal system of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) at room temperature

Figure 1 shows RT-XRD patterns of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) (\( x = 0.00, 0.05, 0.10, 0.15, 0.20 \)) obtained with CuK\( \alpha \) radiation. Three peaks identified as 040, 224 and 400 were observed in 20 range of 67-69° in diffraction pattern of \( \text{LaGa}_2 \) (Fig. 1 (B)), indicating crystal structure was orthorhombic distorted perovskite. All the diffraction peaks of \( \text{LaGa}_2 \) in the range of 20-80° depicted in Fig. 1 (A) could be successfully indexed assuming primitive orthorhombic, showing agreement with previous studies.\textsuperscript{17,12} RT-XRD patterns of Mg\textsuperscript{2+}-substituted \( \text{LaGa}_2 \) as shown in Fig. 1 (A) were almost identical with that of \( \text{LaGa}_2 \)\textsuperscript{20} and systematic peak shift to lower Bragg angle was observed with increase of Mg content, indicating that Mg\textsuperscript{2+} could be substituted for Ga\textsuperscript{3+} site without variation of crystal structure. However, it was observed that full width at half maximum (FWHM) of the peaks depicted in Fig. 1 (B) increased with increase of Mg content from 0.00 to 0.10 and decreased for Mg content more than 0.10. Especially, the FWHM of the peaks of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) was so large that it was difficult to determine accurate Bragg angles.

In order to clarify the origin of large FWHM of \( \text{LaGa}_{14}\text{MgO}_{3.8} \). X-ray diffraction measurements using synchrotron radiation were performed and obtained diffraction peaks corresponding to those of Fig. 1 (B) were shown in Fig. 2. Three peaks, originating from orthorhombic distorted perovskite structure, were observed in every diffraction pattern except for that of \( \text{LaGa}_{14}\text{MgO}_{3.8} \). FWHM of the peaks increased with increase of Mg content from 0.00 to 0.10 and decreased with Mg content more than 0.10, showing same tendency depicted in Fig. 1 (B). Figure 3 (A) shows enlarged diffraction peaks of \( \text{LaGa}_{14}\text{MgO}_{3.8} \). Due to high resolution of synchrotron X-ray diffraction measurements, more than three peaks were successfully observed in Fig. 3 (A). At \( d \) spacing indicated by arrows, 6 peaks, part of them appeared as shoulder, were detected. By comparing the peaks with those of \( \text{LaGa}_2 \) and \( \text{LaGa}_{14}\text{MgO}_{3.8} \) depicted in Fig. 3 (B) and (C), respectively, the peaks represented by solid and dashed arrows in Fig. 1 (A) were identified as those of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) with \( x = 0.00 \) and \( x = 0.10 \), respectively, indicating that there exists two-phase region in \( 0.00 < x < 0.10 \) for \( \text{LaGa}_{14}\text{MgO}_{3.8} \) system. The existence of two phase region suggests that some difference between the phase of \( \text{LaGa}_2 \) and that of \( \text{LaGa}_{14}\text{MgO}_{3.8} \) showing correspondence
with existence of LPAPDS in LaGa$_{0.8}$Mg$_{0.2}$O$_{3.95}$.

3. Phase transition behavior of LaGa$_{1-x}$Mg$_x$O$_{3.95}$ evaluated by thermal analyses

In order to construct structural phase diagram, dependence of the structural phase transition behavior from orthorhombic $Pbnm$ (No. 62) to $R3c$ (No. 167) on Mg content is essential. Thermal analyses, such as dilatometry and DSC, are simple and suitable methods for estimation of the phase transition behavior. We have reported the results of dilatometry and DSC for the specimens with $x = 0.00, 0.10$ and 0.20.\textsuperscript{10} In this study, thermal expansion and DSC of the specimens with $x = 0.00, 0.05, 0.10, 0.15$ and 0.20 have been estimated and the effect of LPAPDS on the phase transition behavior has been discussed.

Fig. 1 (A) X-ray diffraction patterns of LaGa$_{1-x}$Mg$_x$O$_{3.95}$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20$) at room temperature obtained using CuK$\alpha$ radiation. (B) Close up of (A) around $2\theta = 67$-$69^\circ$. All diffraction patterns can be indexed as orthorhombic distorted perovskite structure.

Fig. 2 Synchrotron X-ray diffraction peaks of LaGa$_{1-x}$Mg$_x$O$_{3.95}$ ($x = 0.00, 0.05, 0.10, 0.15, 0.20$) in $d$ spacing range from 1.37 Å to 1.39 Å at room temperature.

Fig. 3 (A) Synchrotron X-ray diffraction peaks of LaGa$_{0.8}$Mg$_{0.2}$O$_{3.95}$ in $d$ spacing range from 1.37 Å to 1.39 Å at room temperature. Six peaks were observed as represented by arrows. Comparing the diffraction peaks of (B) LaGa$_{0.8}$O$_{3.95}$ and (C) LaGa$_{0.8}$Mg$_{0.2}$O$_{3.95}$ the peaks represented by solid arrows and dashed arrows can be identified as those of LaGa$_{1-x}$Mg$_x$O$_{3.95}$ with $x = 0.00$ and $x = 0.10$, respectively.
Figure 4 shows thermal expansion and expansion coefficient of (a) LaGaO₃, (b) LaGa₀.₉₅Mg₀.₀₅O₂₉₇₅, (c) LaGa₀.₉₅Mg₀.₁₀O₂₉₅, (d) LaGa₀.₈₅Mg₀.₁₅O₂₉₂₅ and (e) LaGa₀.₈₀Mg₀.₂₀O₂₉₀ measured by using dilatometry. The discrete shrinkage corresponding to the phase transition was observed at 140 °C in LaGaO₃, showing agreement with previous studies. In thermal expansion curves of LaGa₀.₉₅Mg₀.₀₅O₂₉₇₅, LaGa₀.₉₅Mg₀.₁₀O₂₉₅, LaGa₀.₈₅Mg₀.₁₅O₂₉₂₅ and LaGa₀.₈₀Mg₀.₂₀O₂₉₀, discrete volume shrinkage apparently disappeared. However, small anomaly, corresponding to the structural phase transition, was observed in temperature dependence of expansion coefficient of LaGa₀.₈₀Mg₀.₂₀O₂₉₀ and LaGa₀.₇₅Mg₀.₂₅O₂₉₂₅ at 140 °C, 410 °C, 550 °C and 650 °C, respectively, as depicted by arrows in Fig. 4. For LaGa₀.₇₅Mg₀.₂₅O₂₉₂₅ and LaGa₀.₇₅Mg₀.₂₅O₂₉₀, the temperature where anomaly was observed showed agreement with the results of our previous study. For the specimens with x more than 0.10 where LPAPDS exist, the phase transition temperature increased with increase of Mg content and variation of volume at the phase transition, ΔV, was small. In LaGa₀.₉₅Mg₀.₀₅O₂₉₇₅, this is considered to be a mixture of two phases, showed almost the same transition temperature as that of LaGaO₃ and fair discrete ΔV. This suggests that LaGaₓMg₁₋ₓO₃ with low Mg content and without LPAPDS shows almost constant transition temperature of 140 °C and discrete ΔV.

The phase transition behavior can also be investigated by DSC and obtained DSC curves were shown in Fig. 5. Endothermic peak was observed in DSC curve of LaGaO₃ at 140 °C, where discrete shrinkage was detected in thermal expansion, indicating that the phase transition was the first order. In DSC curves of LaGaₓMg₁₋ₓO₂₉₇₅, small endothermic peak was observed at 140-160 °C, showing correspondence with the conclusion that this phase was composed of two phases, one of which was
LaGa$_{1-x}$Mg$_x$O$_{3.5}$ with $x = 0.00$. In DSC curves of LaGa$_{0.9}$Mg$_{0.1}$O$_{2.95}$, LaGa$_{0.85}$Mg$_{0.15}$O$_{2.95}$ and LaGa$_{0.8}$Mg$_{0.2}$O$_{3.0}$, small and broad endothermic peaks were observed at 410-550°C, 580-650°C and 670-720°C, respectively, showing agreement with phase transition temperature observed by dilatometry. It was concluded that not only $\Delta H$ but also variation of enthalpy at the phase transition, $\Delta H$, was small for LaGa$_{1-x}$Mg$_x$O$_{3.5}$ ($x = 0.10, 0.15, 0.20$) with LPAPDS.

3.3 Analysis of crystal structure of LaGa$_{1-x}$Mg$_x$O$_{3.5}$ at high temperatures by X-ray diffraction

To investigate variation of the crystal structure at the phase transition observed with the thermal analyses, HT-XRD measurements were carried out. Figure 6 and 7 show HT-XRD patterns of LaGa$_{0.1}$ and LaGa$_{0.9}$Mg$_{0.1}$O$_{2.95}$, respectively. If the crystal symmetry is orthorhombic distorted perovskite, three peaks indexed as 040, 224 and 400 should be observed in 20 range of 66.5-69°, whereas two peaks indexed as 220 and 208 of hexagonal description should be detected for rhombohedral distorted perovskite. X-ray diffraction patterns of LaGa$_{0.1}$ at temperature range 30-120°C and 180-800°C could be indexed as primitive orthorhombic symmetry and rhombohedral one, respectively. The diffraction pattern at 150°C could be explained as a mixture of orthorhombic and rhombohedral phase. This temperature agreed with one detected by dilatometry and DSC as shown in Fig. 4 and 5. X-ray diffraction patterns of LaGa$_{0.9}$Mg$_{0.1}$O$_{2.95}$ at temperature range 30-400°C and 550-800°C could be indexed as primitive orthorhombic symmetry and rhombohedral one, respectively. The diffraction pattern at 430-520°C could be explained as a mixture of orthorhombic and rhombohedral phase. Figure 8 shows temperature dependence of molar volume of (A) LaGa$_{0.1}$ and (B) LaGa$_{0.9}$Mg$_{0.1}$O$_{2.95}$, which was calculated from Bragg angles depicted in Fig. 6 (B) and Fig. 7 (B), respectively. The $\Delta V$ of about $-0.083$ cm$^3$/mol corresponding to the first-order phase transition was observed at 140°C in LaGa$_{0.1}$, showing agreement with the result of dilatometry. The smaller $\Delta V$ was observed at 400-550°C in LaGa$_{0.9}$Mg$_{0.1}$O$_{2.95}$, which also showed agreement with thermal expansion behavior observed with dilatometry. The temperature range of LaGa$_{0.9}$Mg$_{0.1}$O$_{2.95}$, where two phases were mixed, was wider than that of LaGa$_{0.1}$, showing agreement with broad variation of expansion coefficient and broad endothermic peak detected by DSC. This also suggests that kinetics of the phase transition of LaGa$_{0.9}$Mg$_{0.1}$O$_{2.95}$ is lower than that of LaGa$_{0.1}$, possibly due to existence of LPAPDS.

Figure 9 shows high temperature X-ray diffraction patterns of LaGa$_{0.9}$Mg$_{0.1}$O$_{2.975}$. Apparently, the diffraction patterns at temperature range of 30-130°C and 400-800°C could be indexed as primitive orthorhombic symmetry and rhombohedral one, respectively; however, it has been concluded that LaGa$_{0.95}$Mg$_{0.05}$O$_{2.975}$ is composed of two kinds of orthorhombic phases at room temperature from synchrotron X-ray diffraction measurement. Therefore, it is necessary to investigate whether

![Fig. 6](image-url)  
(A) X-ray diffraction patterns of LaGa$_{0.1}$ at 30-800°C in 20 range of 20-80°. (B) Close up of (A) around 20 = 67-69°. The diffraction patterns below 120°C can be indexed as primitive orthorhombic, while those above 180°C as rhombohedral symmetry. The diffraction pattern at 150°C can be explained as a mixture of orthorhombic and rhombohedral phase. Description of rhombohedral lattice by hexagonal one is employed in this figure.
LaGa$_{0.25}$Mg$_{0.75}$O$_{2.975}$ is composed of two phases also at high temperatures for construction of phase diagram. Figure 10 shows X-ray diffraction peaks of LaGa$_{1-x}$Mg$_{x}$O$_{2.9}$ (x = 0.00, 0.05, 0.10) at 800°C in 2θ range of 66-69°. For the specimens with x = 0.00 and 0.10, the peaks can be explained as overlapping two peaks, which can be indexed as 220 and 208 of hexagonal description of rhombohedral phase. However, the peaks of LaGa$_{0.85}$Mg$_{0.15}$O$_{2.975}$ cannot be decomposed into only two peaks. As Fig. 10 (B) shows, four peaks were required for curve fitting of diffraction pattern, indicating that LaGa$_{0.15}$Mg$_{0.85}$O$_{2.975}$ was also composed of two phases, one was LaGa$_{1-x}$Mg$_{x}$O$_{2.9}$ with x = 0.00 without LPAPDS and the other x = 0.10 with LPAPDS, even at 800°C and suggesting that LPAPDS exists even in high temperature rhombohedral phase of LaGa$_{1-x}$Mg$_{x}$O$_{2.9}$ with x more than 0.10.

Existence of LPAPDS can also be speculated from FWHM of X-ray diffraction peaks. Figure 11 shows tem-

![Fig. 7](image1.png)  
**Fig. 7** (A) X-ray diffraction patterns of LaGa$_{0.985}$Mg$_{0.015}$O$_{2.95}$ at 30-800°C. (B) close-up of (A) around 2θ = 66.5-68.5°. The diffraction patterns below 400°C can be indexed as orthorhombic, while those above 550°C as rhombohedral symmetry. The diffraction pattern at 430-520°C can be explained as a mixture of orthorhombic and rhombohedral phase.

![Fig. 8](image2.png)  
**Fig. 8** Temperature dependence of molar volume of (A) LaGa$_{2.5}$ and (B) LaGa$_{2.5}$. The discrete volume shrinkage corresponding to the first order phase transition, ΔV of ~0.083 cm$^3$/mol, was observed at 140°C in LaGa$_{2.5}$. The ΔV was also observed between 400-550°C in LaGa$_{2.5}$.
Fig. 9 (A) X-ray diffraction patterns of LaGa$_{0.55}$Mg$_{0.45}$O$_{2.95}$ at 30-800 °C. (B) close-up of (A) around 2θ = 67.0-69.0°.

Fig. 10 X-ray diffraction peaks of LaGa$_{1-x}$Mg$_{0.5}$O$_{3-x}$ (x = 0.00, 0.05, 0.10) at 800 °C in 2θ range of 66.0-69.0°. Peaks of LaGa$_{0.5}$O$_{2.95}$ can be explained as overlapping two peaks indexed as 220 and 208 of hexagonal description for rhombohedral phase. Peaks of LaGa$_{0.5}$Mg$_{0.5}$O$_{2.95}$ cannot be decomposed into two peaks. Four peaks are required for curve fitting, indicating that LaGa$_{0.5}$Mg$_{0.5}$O$_{2.95}$ is composed of two phases even in rhombohedral phase at high temperature.

Temperature dependence of FWHM of the CuKa X-ray diffraction peaks of (A) LaGa$_{0.5}$O$_{2.95}$ appeared at 2θ range of 66.5-69.0°. FWHM of the diffraction peaks of LaGa$_{0.5}$O$_{2.95}$ is around 0.10 regardless of temperature. FWHM of the diffraction peaks of LaGa$_{0.5}$Mg$_{0.5}$O$_{2.95}$ with LPAPDS is larger than those of LaGa$_{0.5}$O$_{2.95}$ for all the measurement temperature range. We consider that broad FWHM were observed in the phase with LPAPDS due to the small domain size and that LPAPDS in LaGa$_{0.5}$Mg$_{0.5}$O$_{2.95}$ was maintained even at 800 °C. This consideration showed agreement with above conclusion that two phases exist in LaGa$_{0.5}$Mg$_{0.5}$O$_{2.95}$ for temperature range below 800 °C.

3.4 Phase diagram of LaGa$_{1-x}$Mg$_{0.5}$O$_{3-x}$ system with consideration of LPAPDS

Figure 12 summarizes phase diagram of LaGa$_{1-x}$Mg$_{0.5}$O$_{3-x}$ system considering LPAPDS proposed in this study. This phase diagram is modified one proposed in our proceeding study. For the compositional range with low Mg content, $P6_3/mmm$ (No. 62) and $R3c$ (No. 167) phases without LPAPDS are observed below and above the transition temperature, respectively. Since the kinetics of the phase transition by temperature is high, region with mixture of orthorhombic and rhombohedral phases is not observed. $Pbnm$ (No. 62) and $R3c$ (No. 167) phase with LPAPDS are proposed for the specimen with x larger than 0.10. Due to slow kinetics of the phase transition, region composed of mixture of $Pbnm$ (No. 62) and $R3c$ (No. 167) is observed. The region with x around 0.05 is composed of two phases, one with and the other without LPAPDS, from room temperature to 800 °C.

For development of high oxide ion conducting oxides,
Fig. 11 Temperature dependence of FWHM of 040, 224, 400 peaks of orthorhombic phase and 220, 208 peaks of rhombohedral phase of (A) LaGaO$_3$ and (B) LaGa$_{0.8}$Mg$_{0.2}$O$_{2.95}$.

Fig. 12 Structural phase diagram of LaGa$_{1-x}$Mg$_x$O$_{3.8}$ proposed in this study. For the compositional range with low Mg content, \textit{Pbnm} (No. 62) and \textit{R3c} (No. 167) phases without LPAPDS are observed below and above the transition temperature, respectively. \textit{Pbnm} (No. 62) and \textit{R3c} (No. 167) phase with LPAPDS are proposed for the specimen with \( x \) larger than 0.10. Due to slow kinetics of the phase transition, region composed of mixture of \textit{Pbnm} (No. 62) and \textit{R3c} (No. 167) is observed. The region with \( x \) around 0.05 is composed of two phases, one with and the other without LPAPDS, from room temperature to 800°C.

we consider that LPAPDS should be eliminated. One probable method is Sr$^{2+}$ substitution for La$^{3+}$ site, because theoretical simulation indicates that association of Sr$_{1-x}$ and V$^5$ is low$^{13-15}$ and FWHM of X-ray diffraction peaks of La$_{1-x}$Sr$_x$Ga$_2$Mg$_{3y}$O$_{3.8}$ are reported to be narrower than those of LaGa$_{1-x}$Mg$_{3y}$O$_{3.8}$.$^{10}$ For confirmation of above speculation, selected area and convergent beam electron diffraction measurements are in progress to obtain direct evidence of existence of LPAPDS in La$_{1-x}$Sr$_x$Ga$_2$Mg$_{3y}$O$_{3.8}$.

4 Conclusion

Phase diagram of LaGa$_{1-x}$Mg$_x$O$_{3.8}$ with consideration of long-period anti-phase domain structure (LPAPDS) has been constructed by using synchrotron X-ray diffraction, high temperature X-ray diffraction and thermal analyses. For the specimens with \( x = 0.00 \), orthorhombic phase with space group of \textit{Pbnm} (No. 62) and rhombohedral phase with \textit{R3c} (No. 167) were detected. No LPAPDS
was observed in the both phases. For LaGa$_{1.5}$Mg$_{0.5}$O$_{3.5}$ with $x$ more than 0.10, orthorhombic phase with LPAPDS was observed and structural phase transition to rhombohedral phase with LPAPDS with increase of temperature was proposed. Two phase region composed of orthorhombic and rhombohedral phase was observed possibly due to slow kinetic of the phase transition in LaGa$_{1.5}$Mg$_{0.5}$O$_{3.5}$ with $x$ more than 0.10. The region with $x$ around 0.05 is composed of two phases, one with and the other without LPAPDS, from room temperature to 800 C.

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References
20) Apparently, the peaks with $h + k + l = odd$ disappeared in the X-ray diffraction patterns of Mg$^{2+}$-substituted LaGaO$_3$ system. However, space group of LaGa$_{1.5}$Mg$_{0.5}$O$_{3.5}$ ($x = 0.00-0.20$) is $Pbnm$ at room temperature and the apparent disappearance of the peaks is due to deficient sensitivity of X-ray diffraction apparatus as indicated in ref. (12).