

Structural effect for Fe-doping in $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

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Local structure of Fe doped lanthanum gallate, LaGaO_3 , has been studied by total neutron scattering technique. In the radial distribution functions, $RDF(r)$, of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$, a peak that corresponds to the M–O correlation in $[\text{MO}_6]$ octahedron (M = $\text{Ga}_{1-x}\text{Fe}_x$) could separate into two signals of the $\text{Ga}^{3+}\text{--O}^{2-}$ and the $\text{Fe}^{3+}(\text{HS})\text{--O}^{2-}$ ones, where HS stands for a high-spin state ($t_{2g}^3e_g^2$). The correlation lengths of the $\text{Ga}^{3+}\text{--O}^{2-}$ and $\text{Fe}^{3+}(\text{HS})\text{--O}^{2-}$ are maintained constant of $\sim 1.985 \text{ \AA}$ and $\sim 2.02 \text{ \AA}$ at all Fe-contents. This result may lead to the conclusion that the distance in the diffusion pathway of oxygen ions around Ga does not change by a substitution of Ga with Fe.

Key words: lanthanum gallate, oxygen ionic conductor, local structure, neutron scattering

1. INTRODUCTION

Lanthanum gallate (LaGaO_3) that has a distorted perovskite-type structure with a three-dimensional network of corner-sharing $[\text{GaO}_6]$ octahedron is well known as an oxygen-ion conductor. For further improvement of the oxygen ionic conductivity, a substitution of trivalent ions, La^{3+} and Ga^{3+} , with bivalent ones (ex. Sr^{2+} and Mg^{2+}) that creates oxygen vacancies has been performed frequently. Indeed, $(\text{La,Sr})(\text{Ga,Mg})\text{O}_{3-\delta}$ shows higher oxygen ionic conductivity close to yttria-stabilized zirconia (YSZ) [1-6]. From the viewpoint of industrial applications, the oxygen-ion conductors based on LaGaO_3 have attracted much interest as electrochemical devices at middle-temperature range ($600 \sim 800^\circ\text{C}$) such as solid oxide fuel cells (SOFCs), oxygen separation membranes and gas sensors [7].

Recently, it has been reported that the oxygen ionic conductivity increases with doping small amount of transition metal elements (ex. Fe, Ni and Co) for $(\text{La,Sr})\text{GaO}_{3-\delta}$ [8,9]. Especially, the Fe doped $(\text{La,Sr})\text{GaO}_{3-\delta}$ shows a large oxygen permeation rate in addition to a high chemical stability at wide range of oxygen partial pressures, while the excessive Fe-doping reduces the oxygen ionic conductivity. The anomalous behavior in the oxygen ionic conductivity is still poorly understood [10].

In our previous work that was focused on the structural investigation of the Fe doped LaGaO_3 by taking advantage of neutron powder diffraction and Rietveld methods [11], we suggested that the electronic configuration of the introduced Fe in LaGaO_3 is a high-spin state, $t_{2g}^3e_g^2$, in crystal-field theory, since the volume of the $[\text{MO}_6]$ octahedron (M = $\text{Ga}_{1-x}\text{Fe}_x$) monotonically increases with doping Fe concentration [12]. This result implies the existence of the strong covalency in the $\text{Fe:}e_g\text{--O:}2p$. Therefore, we point out that a lead for understanding the anomalous behavior in the oxygen ionic conductivity is to clarify the variation of the Ga–O

and the Fe–O correlations attributed the Fe-doping. Although the Rietveld analysis can extract average structure from Bragg reflections, no local structure can directly be examined.

In this work, we carried out time-of-flight neutron powder diffraction experiments with $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. The aim of this investigation is to clarify the local structure of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ using a total scattering technique.

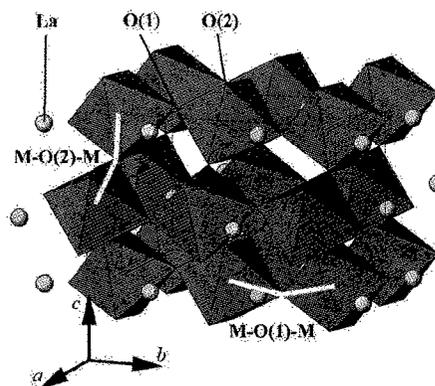


Fig. 1 Crystal structure of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at RT. The gray octahedra consist of $[\text{MO}_6]$ (M = $\text{Ga}_{1-x}\text{Fe}_x$).

2. EXPERIMENTAL

Four polycrystalline samples of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 0, 0.1, 0.25$ and 0.5) were synthesized by conventional solid-state reaction method, as reported elsewhere [12]. As shown in Fig. 1, the crystal structure of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at room temperature (RT) has been refined as an orthorhombic phase (space group: $Pnma$) at all Fe-contents. For these samples, the local structure of

$\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ was investigated using the high intensity total scattering spectrometer (HIT-II), installed at Neutron Science Laboratory (KENS) in High Energy Accelerator Research Organization (KEK). These samples were put into vanadium cylindrical cells. The intensity data of the sample were corrected for background, absorption, multiple and incoherent scatterings. Then, the radial distribution function, $RDF(r)$, was derived from the Fourier transformation of the structure factor, $S(Q)$, up to 45 \AA^{-1} , where Q is a momentum transfer ($= 4\pi \sin\theta / \lambda$).

3. RESULTS

Figure 2 shows $S(Q)$ s for $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$. In the Fourier transformation of the $S(Q)$, the $RDF(r)$ is defined as follows:

$$RDF(r) = 4\pi r^2 \rho_0 g(r), \quad (1)$$

$$g(r) = 1 + \frac{1}{2\pi^2 r \rho_0} \int_0^\infty Q \{S(Q) - 1\} \sin(Qr) dQ, \quad (2)$$

where $g(r)$ is a pair distribution function. The average number density of atoms (ρ_0 in atoms/ \AA^3) for each sample was calculated on the basis of the unit-cell volume and the oxygen deficiencies refined in the Rietveld analysis, as summarized in Table 1. The obtained $RDF(r)$ s for $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ are shown in Fig. 3. The vertical marks above the $RDF(r)$ profiles indicate correlation lengths between atoms. In particular, the first peak at around 2 \AA corresponds to the M-O correlation in the $[\text{MO}_6]$ octahedron.

In order to study the M-O correlation in detail, the profile analysis for the first peak was performed. The first step in evaluating the M-O correlation is to employ the least squares method using a Gaussian distribution. The Gaussian distribution can be written in the form:

$$I_{M-O}(r) = A_{M-O} \exp \left\{ -4 \ln 2 \frac{(r - r_{M-O})^2}{(FWHM_{M-O})^2} \right\}, \quad (3)$$

where A_{M-O} is an amplitude of Gaussian distribution, r_{M-O} is a correlation length, $FWHM_{M-O}$ is a full-width at half-maximum. In this preliminary profile analysis, it was revealed that the r_{M-O} and the $FWHM_{M-O}$ increase with doping Fe. Therefore, we can safely conclude that the first peak includes two components: the Ga-O and the Fe-O correlations. In the subsequent profile analysis, we assumed the following equation with two Gaussian distributions, that is,

$$I_{M-O}(r) = I_{Ga-O}(r) + I_{Fe-O}(r) \\ = A_{Ga-O} \exp \left\{ -4 \ln 2 \frac{(r - r_{Ga-O})^2}{(FWHM_{Ga-O})^2} \right\} + A_{Fe-O} \exp \left\{ -4 \ln 2 \frac{(r - r_{Fe-O})^2}{(FWHM_{Fe-O})^2} \right\}. \quad (4)$$

For all data, the $FWHM_{Ga-O}$ and the $FWHM_{Fe-O}$ were fixed at the same value obtained from the result of the profile analysis on $\text{LaGaO}_{3-\delta}$ ($FWHM = 0.1664 \text{ \AA}$, see Fig. 4 (a)). The A_{Ga-O} and the A_{Fe-O} could be determined by

Table I Principal parameters in the local structure analysis of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$

x	ρ_0	c_{Ga}	c_{Fe}	$\langle b \rangle$
0	0.08445	0.2012	—	6.592
0.1	0.08371	0.1820	0.0202	6.640
0.25	0.08375	0.1512	0.0504	6.702
0.5	0.08231	0.1015	0.1015	6.819

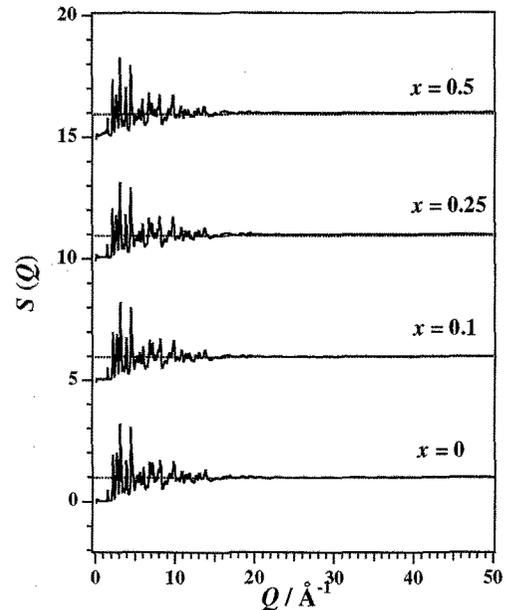


Fig. 2 Structure factors, $S(Q)$, of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at RT. The broken lines indicate $S(Q) = 1$.

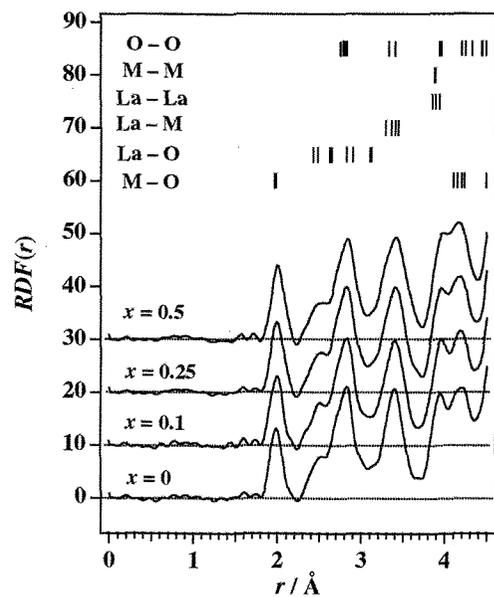


Fig. 3 Radial distribution functions, $RDF(r)$, of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at RT. The vertical marks above the $RDF(r)$ profiles indicate the correlation lengths between atoms. The broken lines indicate $RDF(r) = 0$.

the following processes; Firstly, the integration of Gaussian distributions ($W_{\text{Ga-O}}$ and $W_{\text{Fe-O}}$) is simply represented as a function of the amplitude and the FWHM,

$$W_{\text{Ga-O}} = \int_{-\infty}^{\infty} I_{\text{Ga-O}}(r) dr = A_{\text{Ga-O}} \sqrt{\frac{\pi \cdot (\text{FWHM})^2}{4 \ln 2}}, \quad (5-a)$$

$$W_{\text{Fe-O}} = \int_{-\infty}^{\infty} I_{\text{Fe-O}}(r) dr = A_{\text{Fe-O}} \sqrt{\frac{\pi \cdot (\text{FWHM})^2}{4 \ln 2}}. \quad (5-b)$$

Next, the coordination numbers, $n_{\text{Ga-O}}$ and $n_{\text{Fe-O}}$, are defined by the equations:

$$n_{\text{Ga-O}} = \frac{1}{\xi} \frac{W_{\text{Ga-O}} \langle b \rangle^2}{c_{\text{Ga}} b_{\text{Ga}} b_{\text{O}}}, \quad n_{\text{Fe-O}} = \frac{1}{\xi} \frac{W_{\text{Fe-O}} \langle b \rangle^2}{c_{\text{Fe}} b_{\text{Fe}} b_{\text{O}}} \quad (\xi = 2), \quad (6-a, b)$$

where c_{Ga} and c_{Fe} are concentration of Ga and Fe ions, b_{Ga} ($= 7.288$ fm), b_{Fe} ($= 9.45$ fm) and b_{O} ($= 5.803$ fm) are coherent scattering length for Ga, Fe and O, $\langle b \rangle$ is an average value of b on $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ (see Table I). It is noteworthy that the $n_{\text{Ga-O}}$ and the $n_{\text{Fe-O}}$ are almost 6, because the oxygen deficiency is slight ($\delta < 0.08$). Finally, the $A_{\text{Ga-O}}$ and the $A_{\text{Fe-O}}$ can be described as follows:

$$A_{\text{Ga-O}} = \frac{\xi n_{\text{Ga-O}} c_{\text{Ga}} b_{\text{Ga}} b_{\text{O}}}{\langle b \rangle^2} \sqrt{\frac{4 \ln 2}{\pi \cdot (\text{FWHM})^2}}, \quad (7-a)$$

$$A_{\text{Fe-O}} = \frac{\xi n_{\text{Fe-O}} c_{\text{Fe}} b_{\text{Fe}} b_{\text{O}}}{\langle b \rangle^2} \sqrt{\frac{4 \ln 2}{\pi \cdot (\text{FWHM})^2}}. \quad (7-b)$$

As can be seen from Figs. 4 (a), (b), (c) and (d), excellent fits between the observed and the calculated patterns were obtained. Consequently, the first peak of the M-O correlation could separate into the signals of the Ga-O and the Fe-O ones, and it was found that the correlation length of the Fe-O is larger than that of the Ga-O. The refined $r_{\text{Ga-O}}$ and $r_{\text{Fe-O}}$ are plotted vs. the amount of Fe in Fig. 5. It seems that the $r_{\text{Ga-O}}$ remains constant of ~ 1.985 Å at all Fe-contents. Also, the variation of the $r_{\text{Fe-O}}$ is fairly slight. The average $r_{\text{Fe-O}}$ value is approximately 2.02 Å.

For evaluation of the valences for Ga- and Fe-ions, the bond valence parameter that relates bond valences and bond lengths (Zachariasen-Brown-Altermatt formula) is beneficial [13]. Since most $[\text{MO}_6]$ octahedra have six M-O bonds, the valences of Ga and Fe, V_{Ga} and V_{Fe} , are defined as follows:

$$V_{\text{Ga}} = 6 \exp\left\{\left(l_{\text{Ga-O av.}} - l_{\text{Ga-O}}\right)/B\right\}, \quad (8-a)$$

$$V_{\text{Fe}} = 6 \exp\left\{\left(l_{\text{Fe-O av.}} - l_{\text{Fe-O}}\right)/B\right\}, \quad (8-b)$$

where $l_{\text{Ga-O}} = 1.730$ Å, $l_{\text{Fe-O}} = 1.759$ Å and $B = 0.37$ Å. Inserting the average correlation lengths for the Ga-O ($l_{\text{Ga-O av.}} = 1.985$ Å) and the Fe-O ($l_{\text{Fe-O av.}} = 2.02$ Å) in (8-a) and (8-b) gives the V_{Ga} and the V_{Fe} , which were estimated to be 3.01 and 2.96, respectively. These valence values are consistent with 3+, expected from the

neutrality condition. Therefore, we can say that the $\text{Ga}^{3+}\text{-O}^{2-}$ and the $\text{Fe}^{3+}\text{-O}^{2-}$ correlation lengths that remain stable at ~ 1.985 Å and at ~ 2.02 Å for all Fe-contents are normal in oxides.

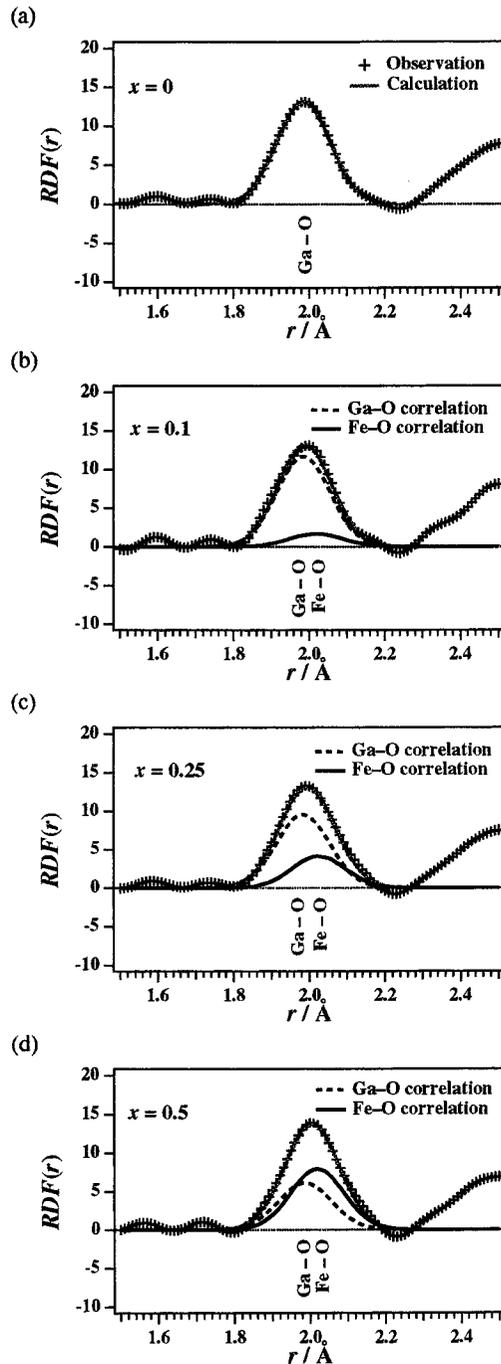


Fig. 4 M-O (M = Ga, Fe) correlation peaks in the $\text{RDF}(r)$ pattern of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ at RT: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.25$ and (d) $x = 0.5$. The plus marks are obtained $\text{RDF}(r)$ s, and the gray solid lines are calculated ones. The components of the Ga-O and the Fe-O correlations are shown as black broken lines and black solid lines, respectively.

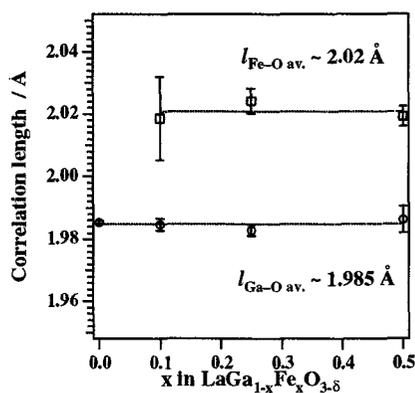


Fig. 5 Variation of the correlation lengths for the Ga–O and the Fe–O as a function of x which is a Fe-content. The broken lines indicate an average value of the correlation length for each correlation.

4. DISCUSSION

In the oxygen-ion conductor based on LaGaO_3 , it has been suggested that the diffusion pathway of oxygen ions is shown as an arc of a circle above edges of corner-sharing $[\text{GaO}_6]$ octahedron [14–16]. Accordingly, the anomalous behavior of the oxygen ionic conductivity on the Fe doped (La,Sr) GaO_3 may be caused by the difference in the covalency of Ga–O and Fe–O correlations. In the local structure analysis, it was revealed that the correlation length of $\text{Fe}^{3+}\text{--O}^{2-}$ is larger than that of $\text{Ga}^{3+}\text{--O}^{2-}$. It means that the electronic configuration of Fe^{3+} has a high-spin state (HS), $t_{2g}^3e_g^2$. The introduction of Fe^{3+} (HS) induces the increase of the free volume as well as that of the unit-cell volume, while oxygen ions would be localized around Fe^{3+} (HS) rather than Ga^{3+} because of the existence of the strong covalency in the $\text{Fe}^{3+}:e_g\text{--O}^{2-}:2p$. If more oxygen vacancies are introduced in the Fe doped LaGaO_3 , they may concentrate around Ga^{3+} . Presumably, when the optimum amount of Fe ($x \sim 0.3$) exists for the higher oxygen ionic conductivity, many oxygen ions immigrate to the oxygen vacancies concentrated around Ga. The distance between the diffusion pathway of the oxygen ions and the Ga^{3+} may remain stable at $\sim 1.985 \text{ \AA}$ for all Fe-contents. In contrast, in the case of the Ga:Fe concentration rate that is comparable, it seems that the most oxygen atoms are localized around Fe^{3+} ; therefore the oxygen ionic conductivity may decrease with the excessive Fe concentration.

5. CONCLUSION

The local structure of the Fe doped LaGaO_3 has been studied by time-of-flight neutron powder diffraction. The $RDF(r)$ s of $\text{LaGa}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ were obtained by the Fourier transformation of the $S(Q)$ s. In the $RDF(r)$, a peak corresponding to M–O correlation in $[\text{MO}_6]$ octahedron ($M = \text{Ga}_{1-x}\text{Fe}_x$) was observed. The profile of the M–O correlation could separate into two pairs: $\text{Ga}^{3+}\text{--O}^{2-}$ and $\text{Fe}^{3+}\text{--O}^{2-}$ correlations. Since the correlation length of the $\text{Fe}^{3+}\text{--O}^{2-}$ is larger than that of the $\text{Ga}^{3+}\text{--O}^{2-}$, the introduced Fe^{3+} has the electronic configuration of the high-spin state, $t_{2g}^3e_g^2$. Furthermore, it was found that the correlation length of the $\text{Ga}^{3+}\text{--O}^{2-}$ is

maintained constant of $\sim 1.985 \text{ \AA}$ at all Fe-contents. This result may lead to the important conclusion that the distance in the diffusion pathway of oxygen ions around Ga does not change by a substitution of Ga with Fe.

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