Dependence of crystal symmetry, electrical conduction property and electronic structure of LnFeO$_3$ (Ln: La, Pr, Nd, Sm) on kinds of Ln$^{3+}$

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Dependence of crystal symmetry, electrical conductivity, chemical state of Fe and optical property of LnFeO$_3$ (Ln: La, Pr, Nd, Sm) on kinds of Ln$^{3+}$ was investigated. All the LnFeO$_3$ showed orthorhombic structure, with which order of high crystal symmetry was LaFeO$_3$ > PrFeO$_3$ > NdFeO$_3$ > SmFeO$_3$. Using tolerance factor, the order was successfully explained. The electrical conductivity of all the specimens could be explained by using small polaron hopping model. With increasing crystallite symmetry, electrical conductivity and activation energy for hopping conduction decreased. This can be ascribed to larger overlapping of Fe$^3$d orbital and O$^2$p orbital on nearly linear Fe–O bond in LnFeO$_3$ with higher crystal symmetry. The larger overlapping of Fe$^3$d orbital and O$^2$p orbital in LnFeO$_3$ with higher crystal symmetry can also be an origin of larger spin–spin interaction detected by Mössbauer spectroscopy and larger optical band gap observed by diffuse reflectance spectroscopy. Since chemical state of Fe, evaluated by Mössbauer spectroscopy, in LnFeO$_3$ is fundamentally constant at +3 regardless of kinds of Ln$^{3+}$, carrier concentration of LnFeO$_3$ was revealed to be constant. It is concluded that the predominant factor which determine the electrical property of LnFeO$_3$ is mobility affected by crystal symmetry.

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1. Introduction

Perovskite-type oxides, LnFeO$_3$ (Ln: lanthanoid) have been utilized as materials for various electrochemical devices such as gas sensor, catalysis, oxygen permeation membrane and fuel cells due to high electrical conductivity and high thermodynamic stability.$^{1,2,3}$ Especially, one of the perovskite-type ferrite oxides, (La,Sr)(Fe,Co)O$_3$ has widely been used as cathode material of solid oxide fuel cells.$^{3,7,10}$ So far, LnFeO$_3$ has frequently employed as material for such electrochemical devices mainly because of low raw material cost of La$_2$O$_3$ comparing with Pr$_6$O$_{11}$, Nd$_2$O$_3$ and Sm$_2$O$_3$. So, there have been few reports in which dependence of electrical conduction property, catalytic activity and other functional property on kinds of lanthanoid ion of LnFeO$_3$ is investigated.

The crystal structure of perovskite-type oxides, whose composition formula can be described as ABO$_3$, is framed with A-site cation and octahedron consisted of B-site cation and oxide ion. The B-site cation and oxide ion are bound with strong covalent chemical bond and A-site cation and the octahedron are connected with strong ionic chemical bond. The main factor which dominates the electrical conduction properties is the overlapping of valence orbital of B-site cation and 2p orbital of oxide ion. The orbital overlapping is affected by bonding length and angle of B–O–B, which are determined by crystal structure. It is recognized that A-site cation affects the symmetry of crystal structure owing to large ionic radius and coordination number. Therefore, it is probable that not only crystal symmetry but also electrical function of LnFeO$_3$ can be controlled by variation of kinds of Ln, resulting in development of materials with superior property.

In this study, crystal structure and electrical property of LnFeO$_3$ (Ln: La, Pr, Nd, Sm) were evaluated. The origin of variation of electrical property and electronic structure by kinds of Ln was investigated utilizing Mössbauer spectroscopy and optical reflection spectroscopy.

2. Experimental

LnFeO$_3$ (Ln = La, Pr, Nd, Sm) were prepared by Pechini method.$^{11}$ La$_2$O$_3$, Pr$_6$O$_{11}$, Nd$_2$O$_3$ or Sm$_2$O$_3$ were employed as raw materials and dissolved with mixture of dilute nitric acid and hydrogen peroxides solution. Before weighing, accurate oxygen content of Pr$_6$O$_{11}$ was estimated by EDTA-chelate titration technique. Fe(NO$_3$)$_3$·9H$_2$O, purity of which was evaluated from the weight of Fe$_2$O$_3$ prepared by heating them at 1000°C for more than 16h in air, was employed as Fe source and dissolved by distilled water. The solutions were mixed with stoichiometric cation ratio. After addition of citric acid and ethylene glycol, which were added to keep homogeneous distribution of cations in the solution during the solvent evaporation by preparation of
polymerized complex;\(^\text{(12)-(13)}\) the solution was heated at 450°C with mantle heater until fired. Obtained precipitate was calcined at 750°C for 24 h and sintered at 1000°C for 10 h. The formation of the single phase for the obtained samples was confirmed with X-ray diffraction (XRD) measurements (RINT-2500, Rigaku Co. Ltd.,) whose power output was 50 kV and 250 mA with Cu Kα. Lattice constants and molar volumes of LnFeO\(_3\) after sintering were also estimated from XRD patterns.

For the electrical conduction measurements, the sintered bodies were prepared by pressing powders into pellets with diameter and length of 5 mm and about 12 mm, respectively, at 200 MPa and sintering at 1200°C in air. Electrical conductivity was measured between 300 and 800°C in air with direct-current four probe technique. As an electrode and lead, Pt pastes and wires were employed, respectively.

Chemical state of Fe ion was evaluated by Mössbauer spectroscopy with γ-ray with 14.4 eV from \(^{57}\)Co/Rh foil at room temperature. Curve fitting using Lorentz function was carried out on the spectra for the estimation of isomer shift, \(\delta\) and internal magnetic field, \(H_i\) with originally manufactured program. The isomer shift, \(\delta\) was expressed with respect to the centroid of the α-Fe.

For the evaluation of optical band gap, \(E_g\) diffuse reflectance spectra were measured at room temperature between 200 and 1000 nm at interval of 1 nm using JASCO V-670 UV–VIS spectrometer. Scanning rate was 400 nm/min. As a light source, D2 lamp and W lamp were employed for wavelength range shorter than and longer than 340 nm, respectively.

3. Results and discussion

3.1 Crystal symmetry of LnFeO\(_3\)

Figure 1 depicts relationship between ionic radius of Ln\(^{3+}\) and tolerance factor, \(t\), calculated as following.

\[
t = \frac{r_{\text{Fe}} + r_{\text{O}}}{\sqrt{2r_{\text{Fe}}r_{\text{O}}}}
\]

Here, \(r_{\text{Fe}}, r_{\text{O}}\) represent ionic radius of 12-coordinated Ln\(^{3+}\) on A-site, 6-coordinated Fe\(^{3+}\) ion on B-site and oxide ion, respectively, proposed by Shannon.\(^\text{(14)}\) It is generally recognized that the symmetry of crystal structure becomes higher as the tolerance factor approaches 1. Since Fig. 1 shows that tolerance factor approaches 1 with increasing \(r_{\text{Fe}}\), it can be prospected that order of high crystal symmetry of LnFeO\(_3\) should be La\(^{3+}\) > Pr\(^{3+}\) > Nd\(^{3+}\) > Sm\(^{3+}\).

Figure 2 shows XRD patterns of LnFeO\(_3\) (Ln = La, Pr, Nd, Sm) after sintering. All the XRD peaks could be indexed as \(Pnma\) (No. 62) orthorhombic symmetry, and no peak identified as second phase was observed. It was suggested that crystal symmetry of LaFeO\(_3\) was the highest among examined LnFeO\(_3\) since peak splitting observed in high 2\(\theta\) range representing low crystal symmetry was smallest for LaFeO\(_3\).

In order to evaluate crystal symmetry, lattice constants and molar volume were calculated using Bragg angle of the peaks with Miller index of 123, 042, 240, 321, 004, 242, 400 and 401.

Figure 3(a) shows the relationship between the ionic radii of Ln\(^{3+}\) (Ln = La, Pr, Nd, Sm) and molar volume, \(V_m\). For comparison, molar volumes estimated from the lattice constants reported in the preceding papers are shown in this figure.\(^\text{(15)-(20)}\) Although some deviations were observed, our obtained \(V_m\) showed fair correspondence with \(V_m\) reported in the preceding reports. The molar volume increased almost linearly with increasing ionic radii of Ln\(^{3+}\), indicating LnFeO\(_3\) was successfully prepared. For orthorhombic perovskite with space group of \(Pnma\) (No. 62), length of \(a, b\) and \(c\) are represented as \(a \approx \sqrt{2}a_p, b \approx 2a_p\) and \(c \approx \sqrt{2}a_p\), respectively. Here, \(a_p\) denotes lattice constant of ideal cubic perovskite structure. Therefore, it can be prospected that difference of the reduced lattice constants, i.e., \(a/\sqrt{2}, b/2\) and \(c/\sqrt{2}\) should be smaller with increasing crystal symmetry. Figure 3(b) shows the relationship between tolerance factor of LnFeO\(_3\) and the reduced lattice constants. The difference of the reduced lattice constants became smaller with tolerance factor approaching 1. In order to evaluate the crystal symmetry in more detail, the bond length between Fe–O and the bond angle of Fe–O–Fe in direction of \(b\)-axis were estimated from the lattice parameters in this study and the atomic coordinate reported in the preceding papers\(^\text{(11)-(21)}\) using the visualization software, VESTA.\(^\text{24)}\) Figure 3(c) shows the relationship between tolerance factor and these values. The bond length of Fe–O is approximately 2.0 Å, which is independent on the tolerance factor. On the other hand, the bond angle of Fe–O–Fe approaches 180° with tolerance factor approaching 1, indicating that the prospect from Fig. 1 that order of high crystal symmetry of LnFeO\(_3\) should be La\(^{3+}\) > Pr\(^{3+}\) > Nd\(^{3+}\) > Sm\(^{3+}\) is satisfied and that tolerance factor can be a good index for the evaluation of...
3.2 Electrical conduction property of LnFeO$_3$

Small hopping conduction model is represented as Eq. (2).

$$\sigma \propto \mu = A_0 \exp\left(-\frac{E_a}{kT}\right)$$  \hspace{1cm} (2)

Here, $\sigma$, $\mu$, $A_0$, $T$, $E_a$ and $k$ are electrical conductivity, carrier mobility, frequency factor, temperature, activation energy for hopping conduction and Boltzmann constant, respectively. Therefore, small polaron hopping conduction model can be applicable if the linear relationship is observed between $\ln(\sigma T)$ and $1/T$.

Figure 4(a) shows dependence of $\ln(\sigma T)$ of LnFeO$_3$ on reciprocal of temperature. Linear relationship with R-squared values of more than 99% was observed for every specimen, indicating that the small polaron hopping conduction model was applicable. Figure 4(b) shows the relationship among tolerance factor, electrical conductivity at 600°C in air and $E_a$ of LnFeO$_3$ evaluated from the slopes of Fig. 4(a). Electrical conductivity increased and $E_a$ decreased with tolerance factor approaching 1. The decrease of $E_a$ shows correspondence with variation of crystal symmetry described in chapter 3.1. Since it is prospected that bond angle of Fe–O–Fe approaches 180° with tolerance factor approaching 1, it is expected that overlapping of Fe$^{3d}$ and O$^{2p}$ orbitals should be enhanced, resulting in decrease of $E_a$ and increase of $\sigma$. Another possible origin of variation of $\sigma$ of LnFeO$_3$ by kind of Ln is variation of carrier density; however, it is less possible since partial cation substitution and introduction of oxide ion vacancy to change chemical state of Fe was not carried out. In order to confirm the chemical state of Fe in LnFeO$_3$, Mössbauer spectroscopy measurements were performed.

3.3 Mössbauer spectroscopy of LnFeO$_3$

Figure 5 shows Mössbauer spectra of LnFeO$_3$ at room temperature. The sextet peaks were observed in the spectra of all the
specimens, indicating that magnetic character of LnFeO$_3$ (Ln = La, Pr, Nd, Sm) are antiferromagnetic. Figure 6 shows isomar shift, $\delta$ and internal magnetic field, $H_i$, of LnFeO$_3$ estimated from Mössbauer spectra as a function of tolerance factor. The $H_i$ of LnFeO$_3$ increased with increasing tolerance factor, indicating that spin–spin interaction of electron located at Fe ion is stronger as higher crystallite symmetry. It was suspected that observed stronger spin–spin interaction in LnFeO$_3$ with higher crystal symmetry originates from higher overlapping of Fe3d and O2p orbital due to nearly linear Fe–O–Fe bond. Isomar shift, $\delta$ were constant regardless of the difference of Ln ion in LnFeO$_3$. This indicates that the valence of Fe ion in all the specimens is fundamentally constant at $+3$, resulting in small difference of conduction carrier density among LnFeO$_3$.

### 3.4 Optical property of LnFeO$_3$

The crystal symmetry can affect the optical property. Figure 7(a) shows UV–VIS diffuse reflectance spectra of LnFeO$_3$ at room temperature. For direct allowed transition, optical band gap, $E_g$ can be estimated from the following equation,$^{25,28}$

$$F(R)h\nu = A(\nu - E_g)^2$$

where $h$, $\nu$ and $A$ are Planck constant, the frequency of light and energy-independent constant, respectively. $F(R)$, called Kubelka–Munk equation, can be expressed as following.

$$F(R) = \frac{\alpha}{s} = \frac{(1 - R)^2}{2R}$$

where $\alpha$, $s$ and $R$ are absorption coefficient, scattering factor and reflectance, respectively. Therefore, $F(R)$ can be calculated only from reflectance. Figure 7(b) shows Tauc plot,$^{21}$ which is the relationship between photon energy and $[F(R)h\nu]^2$, of LnFeO$_3$. Linear relationship was observed around 2.0–2.8 eV for every Tauc plot, indicating that $E_g$ can be measured by extrapolation of the observed linear relationship to horizontal axis of Fig. 7(b).

Figure 8 shows the relationship between tolerance factor, $t$, and optical band gap, $E_g$, of LnFeO$_3$. $E_g$ increased with $t$ approaching to unity. It is prospected that the origin of $E_g$ is
splitting of energy level of t2g Fe3d orbital and eg Fe3d orbital in octahedral symmetry. Figure 9 shows the schematic diagram of electronic configuration in the orbitals of [FeO3] octahedron in LnFeO3. Since t2g orbital shows nonbonding character with O2p orbital, influence of crystal symmetry on energy level should be small; On the contrary, energy level of antibonding σ* orbital composed of eg and O2p should be affected by crystal symmetry. In LaFeO3, large overlapping between eg Fe3d orbital and O2p orbital is expected owing to nearly linear Fe–O–Fe bond, resulting in large $E_g$ due to large energy splitting between t2g and $\sigma^*$ orbitals. With decreasing ionic radius of Ln in LnFeO3, the overlapping of eg and O2p becomes smaller due to bending of Fe–O–Fe bond originating from low crystal symmetry, resulting in smaller $E_g$ due to decrease of energy level of $\sigma^*$. Since, $E_g$ of these specimens are 2.1–2.5 eV, which are too high for to generate intrinsic electron carrier under the measurement condition, which shows correspondence with no difference of chemical state of Fe by kinds of Ln in LnFeO3 observed with Mössbauer spectroscopy.

4. Conclusion

Single phase of orthorhombic LnFeO3 (Ln = La, Pr, Nd, Sm) was prepared by Pechini method. The order of high crystal symmetry is LaFeO3 > PrFeO3 > NdFeO3 > SmFeO3, which can be explained with variation of tolerance factor by kind of Ln3+. The electrical conductivity of all the specimens could be explained by using small polaron hopping model. For the specimen with higher crystal symmetry, higher electrical conductivity due to lower activation energy for hopping conduction was observed, which can be ascribed to larger overlapping between Fe3d orbital and O2p orbital on the nearly linear Fe–O–Fe bond. Due to the larger overlapping of Fe3d orbital and O2p orbital, larger internal magnetic field and larger optical band gap was observed for LnFeO3 with larger Ln3+ and higher crystal symmetry. Since valence of Fe evaluated by Mössbauer spectroscopy is almost same among LnFeO3 and optical bad gaps are too high for generation of intrinsic electric carrier, it is prospected that difference of electric carrier concentration in LnFeO3 by kinds of Ln3+ is small. It can be concluded that predominant factor which determines the electrical conduction property of LnFeO3 is mobility affected by crystal symmetry.

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