Rietveld analysis of structure transformation between perovskite-type and B-type rare earth structures

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La₀.₇₆Ln₀.₂₄O₃ (Ln = Dy, Ho, Y, Er, and Yb) and La(Ln, Ln')O₃ (Ln, Ln' = Dy, Ho, Er, and Yb) systems were synthesized by solid state reaction method and characterized by X-ray diffraction and Rietveld analysis. In order to investigate the size effect of Ln site ion in ABO₃-type compound, the phase relationship in the La₀.₇₆Ln₀.₂₄O₃ system. When Ln = Er or Yb which has smaller ionic radius than that of Y³⁺ (0.900 Å), the La₀.₇₆Ln₀.₂₄O₃ showed an orthorhombic perovskite-type structure, while when Ln = Dy or Ho which has larger ionic radius than that of Y³⁺, it showed a monoclinic B-type rare earth structure. Next, the solid solution system of LaHoₓYb₁₋ₓO₃ was investigated in order to clarify the crystallochemical factor affecting the structural transformation. The XRD experiments revealed that the samples with x = 0.90 (ravl=0.8977 Å) showed the orthorhombic perovskite-type structure, changed to the mixed phases of monoclinic B-type rare earth, and orthorhombic perovskite-type structures with increasing x, and then the samples with x ≥ 0.95 (ravl=0.8994 Å) showed the monoclinic B-type rare earth structures, where ravl represents the average ionic radii of Ln and Ln'. Therefore, in order to search into process of phase transformation from orthorhombic perovskite-type structure to monoclinic B-type rare earth structure, LaHoₓYb₁₋ₓO₃ (0.90 ≤ x ≤ 0.95) system was performed Rietveld analysis.

Key words: perovskite-type structure, B-type rare earth structure, ionic radius, Rietveld analysis

1. Introduction

Inasmuch as have properties such as mechanical strength, chemical stability, and high conductivity, which are affect by introduction of defection and size of the space, and etc., fluorite-type related structure (cubic fluorite-type (Fig.1a), cubic pyrochlore-type (Fig.1b) cubic C-type rare earth (Fig.1c), monoclinic B-type rare earth (Fig.1d), and hexagonal A-type rare earth structures (Fig.1e)) and perovskite-type related structure (perovskite-type (Fig.1f), brownmillerite-type (Fig.1g), and rhenium oxide-type structures (Fig.1h)) are paid much attention as electrolytes of solid oxide fuel cell due to their oxide ion conductivities. Among La₀.₇₆Ln₀.₂₄O₃ (Ln: Y or rare earth), LaYO₃ is an interesting compound from the viewpoint of crystal chemistry, because firing at 1400°C showed a low temperature form with orthorhombic perovskite-type structure (Fig.1e), while the firing at 1600°C transformed to the high temperature form with a monoclinic B-type rare earth structure (Fig.1e) [1, 2].

The reason why the structure transformation occurs dependent on the firing temperature has not been apparent. In the present study, in order to investigate the crystallochemical factor effecting on the structure transformation, we focused attention on La₀.₇₆Ln₀.₂₄O₃ and La(Ln, Ln')O₃.

Fig.1 Schematic representation of fluorite-type related structure and perovskite-type structure. (a) Fluorite-type (b) Pyrochlore-type (c) C-type rare earth (d) B-type rare earth (e) A-type rare earth (f) Perovskite-type (g) Brownmillerite-type (h) Rhenium oxide-type
2. Experimental

Powder samples of the present systems, LaLnO$_3$ (Ln = Dy, Ho, Y, Er, Yb), La(Ln, Ln')O$_3$ (Ln, Ln' = Dy, Ho, Er, Yb) were synthesized by means of a solid state reaction method, using La$_2$O$_3$ (99.99%, High Purity Chemicals), Dy$_2$O$_3$, Ho$_2$O$_3$, Y$_2$O$_3$, Er$_2$O$_3$, and Yb$_2$O$_3$ (99.9%, High Purity Chemicals) as starting materials. The weighed powders were wet ball-milled for 24 h, using a milling pot made of synthetic resin and resin-coated balls, and ethanol as dispersion reagent. After drying, the powder mixtures were calcined at 1000°C for 10 h in air. After sieving powders under 53 µm in mesh size, the powder samples were molded under the pressure of 5 MPa and subjected to rubber press at 200 MPa. The compacts thus obtained were sintered at 1400°C and 1600°C for 10 h in air, where the heating and cooling rates were 5 °C/min.

The powdered samples were characterized by means of X-ray diffraction (XRD) (model: MultiFlex, Rigaku) with monochromated CuKα radiation at room temperature. The lattice constant was determined from the XRD peaks by least squares method. In order to carry out the Rietveld analysis, XRD data was collected in the 2θ scanning range from 10° to 140° with a step interval of 0.02° at room temperature. The data was stimulated up to 20000 counts for the strongest diffraction peak. The Rietveld analysis was carried out using the Rietan-FP application software [3].

3. Results and Discussion

Fig. 2 shows XRD patterns of LaYO$_3$ prepared by firing at 1400°C and 1600°C. It was confirmed that LaYO$_3$ showed a low temperature form of orthorhombic perovskite-type structure by firing at 1400°C, while it showed a high temperature form of monoclinic B-type rare earth structure by firing at 1600°C [1]. Then, the samples sintered at 1600°C were annealed at 1400°C for 10 h or 1200°C for 10 h, as shown in Fig. 3. The annealed sample was transformed from the monoclinic B-type rare earth structure to the orthorhombic perovskite-type structure, suggesting the reversible transformation of crystal structure.

Fig. 4 shows Rietveld analysis of XRD data of LaYO$_3$ prepared by firing at 1400°C. The sample was analyzed, assuming the single phase of orthorhombic perovskite-type structure (S.G. : Pnma). The result of Rietveld analysis showed $R_{wp}$=14.8%, and $S$=2.43 suggesting insufficient fitting. Therefore, the sample was again analyzed, assuming two phases of orthorhombic perovskite-type and monoclinic B-type rare earth (S.G. : C2/m) structures. The result showed $R_{wp}$=10.5% and $S$=1.73, which were the lower values compared with the case of single phase. Therefore, it was found that LaYO$_3$ prepared at 1400°C is composed of 96.4% orthorhombic perovskite-type structure and 3.6% monoclinic B-type rare earth structure (Fig. 5).

In order to investigate the size effect of Ln ion, the phase relationship in the La LnO$_3$ (Ln = Dy, Ho, Y, Er, Yb) systems [4], where Ln has a larger or smaller ionic radius than that of Y$^{3+}$, was
investigated. The ionic radii of $Ln^{3+}$ are summarized in Table I [5].

In the LaLnO$_3$ systems, when $Ln = Er$ (0.890 Å) or Yb (0.868 Å) which has the smaller the ionic radius than that of Y$^{3+}$, the sample showed the orthorhombic perovskite-type structure regardless $1400^\circ$C or $1600^\circ$C firing, while when $Ln = Dy$, (0.912 Å) or Ho (0.901 Å) which has larger the ionic radius than that of Y$^{3+}$, it showed the monoclinic B-type rare earth structure regardless the firing temperatures, as shown in Fig. 6 and 7. These facts suggest that the crystal structure of LaLnO$_3$ system strongly depends on the ionic size of $Ln^{3+}$.

In order to investigate in detail the size effect of $Ln^{3+}$ affecting the crystal structure, the solid solution systems of La(Ln, Ln')O$_3$ ($Ln$, $Ln'$ = Dy, Ho, Er, Yb) were investigated, where the composition ratio, $Ln/Ln'$, was controlled for the average ionic radius of $Ln$ and $Ln'$ ($r_{av}$) to be in the vicinity of the ionic radius of Y$^{3+}$. Table II shows the compositional dependence of average ionic radius in the system with $Ln = Ho$ and $Ln' = Yb$.

In the system LaHo$_x$Yb$_{1-x}$O$_3$ ($0.90 \leq x \leq 0.95$), XRD patterns showed mixed phases of the monoclinic B-type rare earth and orthorhombic perovskite-type structures when the samples were sintered at $1400^\circ$C for 10 h. Therefore, the samples were annealed at $1300^\circ$C for 10 h. The samples with $x = 0.90$ ($r_{av} = 0.8977$ Å) showed the orthorhombic perovskite-type structure, and then changed to the mixed phases of the orthorhombic perovskite-type and monoclinic B-type rare earth structures in the composition range, $0.90 < x \leq 0.95$, as shown in Fig. 8. Fig. 9 shows XRD patterns of LaHo$_x$Yb$_{1-x}$O$_3$ system prepared by firing at $1600^\circ$C for 20 h. The samples with $x = 0.90$ ($r_{av} = 0.8994$ Å) showed the monoclinic B-type rare earth structure.

In order to search into process of phase transformation from orthorhombic perovskite-type structure to monoclinic B-type rare earth structure, samples that LaHo$_x$Yb$_{1-x}$O$_3$ ($0.90 \leq x \leq 0.95$) system prepared by firing at $1600^\circ$C for 20 h was performed Rietveld analysis. The samples with $x = 0.90$ and 0.95 are performed analysis of single phase and $0.90 < x < 0.95$ are two phases model. Phases existence ratio of orthorhombic perovskite-type and monoclinic B-type rare earth structures was shown in Table III, respectively. The results obtained by Rietveld analysis were

### Table I  Ionic radius (Å) of $Ln^{3+}$

<table>
<thead>
<tr>
<th>$Ln^{3+}$</th>
<th>Dy$^{3+}$</th>
<th>Ho$^{3+}$</th>
<th>Y$^{3+}$</th>
<th>Er$^{3+}$</th>
<th>Yb$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ionic radius</td>
<td>0.912</td>
<td>0.901</td>
<td>0.900</td>
<td>0.890</td>
<td>0.868</td>
</tr>
</tbody>
</table>

Fig.6 XRD patterns of LaLnO$_3$ prepared by firing at $1400^\circ$C.

Fig.7 XRD patterns of LaLnO$_3$ prepared by firing at $1600^\circ$C.

### Table II  Average ionic radius ($r_{av}$Å) in the LaHo$_x$Yb$_{1-x}$O$_3$ system.

<table>
<thead>
<tr>
<th>$x$</th>
<th>0.95</th>
<th>0.94</th>
<th>0.93</th>
<th>0.92</th>
<th>0.91</th>
<th>0.90</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{av}$</td>
<td>0.8994</td>
<td>0.8990</td>
<td>0.8987</td>
<td>0.8984</td>
<td>0.8980</td>
<td>0.8977</td>
</tr>
</tbody>
</table>

Fig.8 XRD patterns of LaHo$_x$Yb$_{1-x}$O$_3$ firing $1400^\circ$C and annealed at $1300^\circ$C.
plotted phase existence ratio as a function of average ionic radius of (Ln, Ln') site (Fig. 10). With increasing average ionic radius of B site, phase existence ratio was obtained linearly decreasing trend for orthorhombic perovskite-type structure, and it was obtained linearly increasing trend for monoclinic B-type rare earth structure.

Furthermore, LaErHo xO3 system was also produced same as average ionic radius of (Ln, Ln') in LaHo yYb1-xO3 system, and LaErHo xO3 system was performed Rietveld analysis. As a result, when average ionic radius of (Ln, Ln') which has smaller than rB = 0.8977 Å, the sample showed the orthorhombic perovskite-type structure, while when average ionic radius of (Ln, Ln') which has larger than rB = 0.8994 Å, it showed the monoclinic B-type rare earth structure. Therefore, in the La(Ln, Ln')O3 systems, controlling for the average ionic radius of (Ln, Ln'), we could produce the orthorhombic perovskite-type or monoclinic B-type rare earth structures.

4. Conclusion

In the LaLnO3 system, when Ln = Er or Yb which has smaller ionic radius than that of Y (0.900 Å), the samples showed an orthorhombic perovskite-type structure, while when Ln = Dy or Ho which has larger ionic radius than that of Y, it showed a monoclinic B-type rare earth structure. In the LaHo yYb1-xO3 (0.90 ≤ x ≤ 0.95) system, the samples with x = 0.90 showed the orthorhombic perovskite-type structure, and then changed to the mixed phases of the monoclinic B-type rare earth and orthorhombic perovskite-type structures in the composition range, 0.90 < x < 0.95, and when x = 0.95, the sample showed the monoclinic B-type rare earth structure by firing at 1600°C for 20 h. Therefore, the monoclinic B-type rare earth structure was stable when the ionic radius is larger than 0.8994 Å, and the orthorhombic perovskite-type structure was stable when the ionic radius is smaller than 0.8977 Å. Consequently, LaLnO3 (Ln = Dy, Ho, Y, Er, Yb) and La(Ln,Ln')O3 (Ln, Ln' = Dy, Ho, Er, Yb) systems dependent on the ionic size of Ln+ or (Ln, Ln').

Table III Phase existence ratio as a function of average radius of (Ln, Ln') in the LaHo xYb1-xO3 system.

<table>
<thead>
<tr>
<th>x</th>
<th>Average ionic radius of (Ln, Ln') (Å)</th>
<th>Orthorhombic perovskite-type (%)</th>
<th>Monoclinic B-type rare earth (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.95</td>
<td>0.8994</td>
<td>0.0</td>
<td>100</td>
</tr>
<tr>
<td>0.94</td>
<td>0.8990</td>
<td>9.8</td>
<td>90.2</td>
</tr>
<tr>
<td>0.93</td>
<td>0.8987</td>
<td>27.4</td>
<td>72.6</td>
</tr>
<tr>
<td>0.92</td>
<td>0.8984</td>
<td>61.4</td>
<td>38.6</td>
</tr>
<tr>
<td>0.91</td>
<td>0.8980</td>
<td>82.2</td>
<td>17.8</td>
</tr>
<tr>
<td>0.90</td>
<td>0.8977</td>
<td>100</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Fig. 9 XRD patterns of LaHo xYb1-xO3 prepared by firing at 1600°C.

Fig. 10 Phase existence ratio as a function of average ionic radius of (Ln, Ln') in the LaHo xYb1-xO3 system.

- Orthorhombic perovskite-type structure
- Monoclinic B-type rare earth structure

Reference


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