

IUMRS-ICA 2011

Structure Transformation between Perovskite-type and B-type Rare Earth Structures

N. Okita^{1,*}, A. Higashide¹, M. Saito¹, H. Yamamura¹

¹Department of Material and Life Chemistry, Faculty of Engineering, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama, 221-8686, Japan

Abstract

LaLnO_3 ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Y}, \text{Er}, \text{and Yb}$) and $\text{La}(\text{Ln}, \text{Ln}')\text{O}_3$ ($\text{Ln}, \text{Ln}' = \text{Dy}, \text{Ho}, \text{Er}, \text{and Yb}$) systems were synthesized by solid state reaction method and characterized by X-ray diffraction. When $\text{Ln} = \text{Er}$ or Yb which has smaller ionic radius than that of Y^{3+} (0.900Å), the LaLnO_3 showed an orthorhombic perovskite structure, while when $\text{Ln} = \text{Dy}$ or Ho which has larger ionic radius than that of Y^{3+} , it showed a monoclinic B-type rare earth structure. Next, the solid solution system of $\text{LaHo}_x\text{Yb}_{1-x}\text{O}_3$ was investigated in order to clarify the crystallochemical factor affecting the structural transformation. The XRD experiments revealed that the samples with $x = 0.90$ ($r_{\text{av.}}=0.8977\text{\AA}$) showed the orthorhombic perovskite structure, changed to the mixed phases of monoclinic B-type rare earth, and orthorhombic perovskite structures with increasing x , and then the samples with $x \geq 0.95$ ($r_{\text{av.}}=0.8994\text{\AA}$) showed the monoclinic B-type rare earth structures, where $r_{\text{av.}}$ represents the average ionic radii of Ln and Ln' .

© 2011 Published by Elsevier Ltd. Selection and/or peer-review under responsibility of MRS-Taiwan

Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Perovskite-type structure; B-type rare earth structure; ionic radius; Rietveld analysis

1. Introduction

Fluorite-type related structure (cubic fluorite-type (Fig. 1a), cubic C-type rare earth (Fig. 1b), monoclinic B-type rare earth (Fig. 1c), hexagonal A-type rare earth structures (Fig. 1d)) and perovskite-type structure (Fig. 1e) are paid much attention as electrolytes of solid oxide fuel cell due to their oxide ion conductivities. Among LaLnO_3 ($\text{Ln}: \text{Y}$ or rare earth), LaYO_3 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. 1c) [1, 2].

*Corresponding author. Tel.: +81 045 481 4551

E-mail address: o_15_22_41@vahoo.co.jp (N. Okita)

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 LaLnO_3 and $\text{La}(\text{Ln}, \text{Ln}')\text{O}_3$.

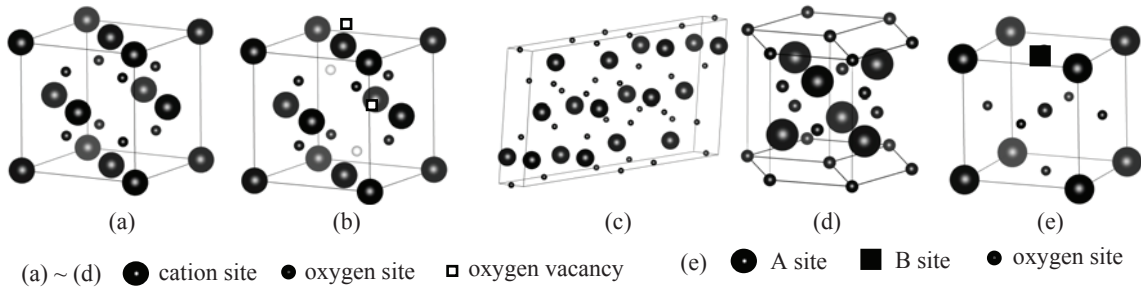


Fig. 1 Schematic representation of fluorite-type related structure and perovskite-type structure. (a) Fluorite-type (b) C-type rare earth (c) B-type rare earth (d) A-type rare earth (e) Perovskite-type

2. Experimental

Powder samples of the present systems, LaLnO_3 ($\text{Ln} = \text{Dy}, \text{Ho}, \text{Y}, \text{Er}, \text{Yb}$), $\text{La}(\text{Ln}, \text{Ln}')\text{O}_3$ ($\text{Ln}, \text{Ln}' = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) were synthesized by means of a solid state reaction method, using La_2O_3 (99.99 %, High Purity Chemicals), Dy_2O_3 , Ho_2O_3 , Y_2O_3 , Er_2O_3 , and Yb_2O_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 $53 \mu\text{m}$ 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 $5^\circ\text{C}/\text{min}$.

The powdered samples were characterized by means of X-ray diffraction (XRD) (model: MultiFlex, Rigaku) with monochromated $\text{CuK}\alpha$ 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 130° 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

Figure 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.

Figure 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 $R_{\text{wp}}=14.8\%$ 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 $R_{wp}=9.4\%$ and $S=1.84$, which were the lower values comparing with the case of single phase. Therefore, it was found that $LaYO_3$ prepared at $1400^\circ C$ is composed of 93.7% orthorhombic perovskite-type structure and 6.3% monoclinic B-type rare earth structure (Fig. 5).

In order to investigate the size effect of Ln ion, the phase relationship in the $LaLnO_3$ ($Ln = Dy, Ho, Y, Er, Yb$) 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 1 [5].

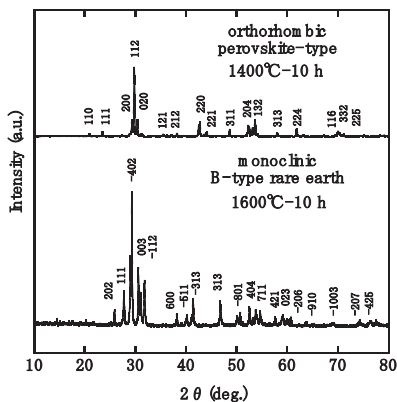


Fig. 2 XRD patterns of $LaYO_3$ prepared by firing at 1400 and $1600^\circ C$.

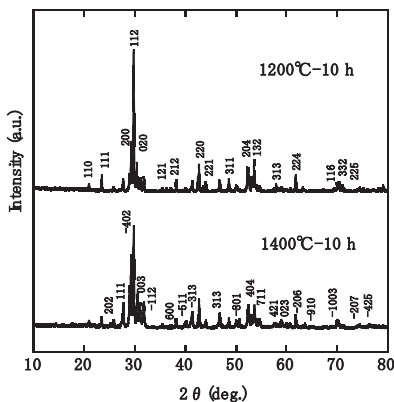


Fig. 3 XRD patterns of $LaYO_3$ annealed at $1400^\circ C$ or $1200^\circ C$, 10 h, after the $1600^\circ C$ sintering.

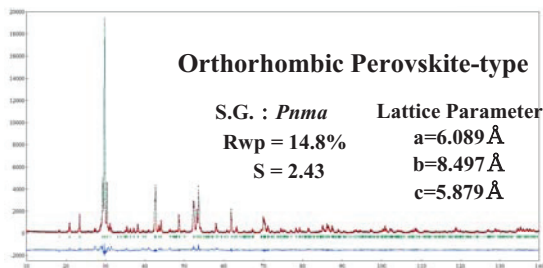


Fig. 4 Rietveld analysis of $LaYO_3$ prepared by firing at $1400^\circ C$. (single phase).

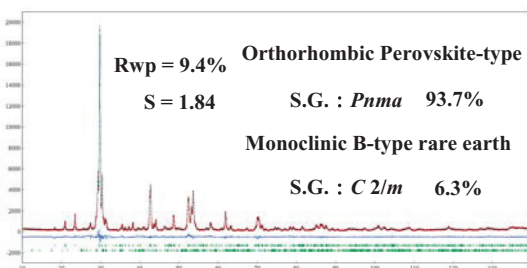


Fig. 5 Rietveld analysis of $LaYO_3$ prepared by firing at $1400^\circ C$. (two phases).

Table 1 Ionic radius (Å) of Ln^{3+} .

| Ln^{3+} | Dy^{3+} | Ho^{3+} | Y^{3+} | Er^{3+} | Yb^{3+} |
|--------------|-----------|-----------|----------|-----------|-----------|
| Ionic radius | 0.912 | 0.901 | 0.900 | 0.890 | 0.868 |

Table 2 Average ionic radius (Å) in the $LaHo_xYb_{1-x}O_3$ system.

| x | 0.95 | 0.94 | 0.93 | 0.92 | 0.91 | 0.90 |
|----------------------|--------|--------|--------|--------|--------|--------|
| Average ionic radius | 0.8994 | 0.8990 | 0.8987 | 0.8984 | 0.8980 | 0.8977 |

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 $\text{La}(\text{Ln}, \text{Ln}')\text{O}_3$ ($\text{Ln}, \text{Ln}' = \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$) 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 2 shows the compositional dependence of average ionic radius in the system with $\text{Ln} = \text{Ho}$ and $\text{Ln}' = \text{Yb}$.

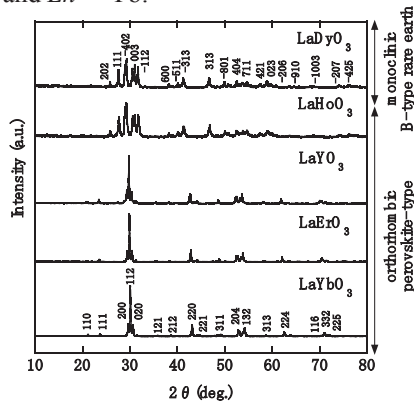


Fig. 6 XRD patterns of LaLnO_3 prepared by firing at 1400°C .

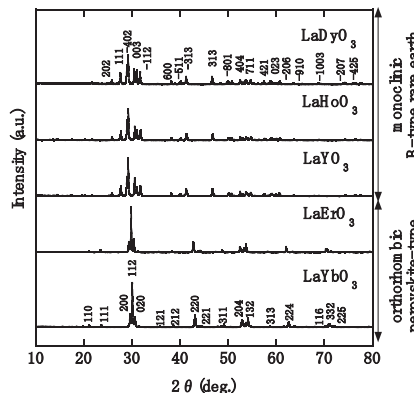


Fig. 7 XRD patterns of LaLnO_3 prepared by firing at 1600°C .

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

4. Conclusions

In the LaLnO_3 system, when $\text{Ln} = \text{Er}$ or Yb which has smaller ionic radius than that of Y (0.900 \AA), the samples showed an orthorhombic perovskite structure, while when $\text{Ln} = \text{Dy}$ or Ho which has larger ionic radius than that of Y , it showed a monoclinic B-type rare earth structure. In the $\text{LaHo}_x\text{Yb}_{1-x}\text{O}_3$ ($0.90 \leq x \leq 0.95$) 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 \AA , and the orthorhombic perovskite-type structure was stable when the ionic radius is smaller than 0.8977 \AA .

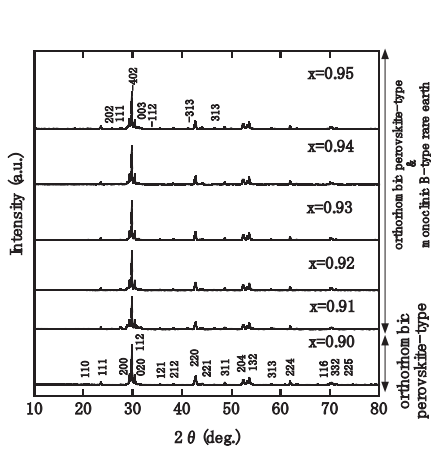


Fig. 8 XRD patterns of $\text{LaHo}_x\text{Yb}_{1-x}\text{O}_3$ sintered 1400 °C and annealed at 1300°C.

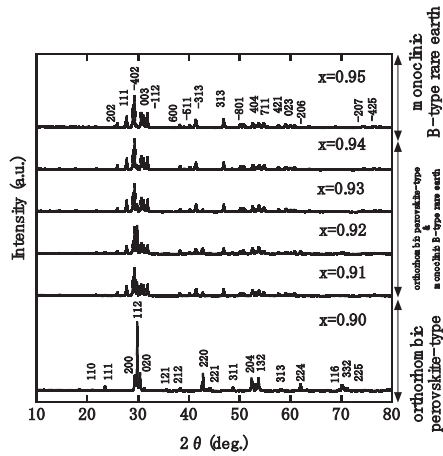


Fig. 9 XRD patterns of $\text{LaHo}_x\text{Yb}_{1-x}\text{O}_3$ prepared by firing at 1600°C.

References

- [1] H. Yamamura, K. Yamazaki, K. Kakinuma, *Solid State Ionics*, **150** (2002) 255-261.
- [2] V. P. Gorelov, Z. S. Martem'yanova, V. B. Balakireva, *Inorganic Materials*, **35** (1999) 153-157.
- [3] F. Izumi and K. Momma, *Solid State Phenimena*, **130** (2007) 15-20.
- [4] C. Artini, G. A. Costa, M. M. Carnasciali, R. Masini, *Journal of Alloys and Compounds*, **494** (2010) 336-339.
- [5] R.D. Shannon, C.T. Prewitt, *Acta Crystallographica*, **B25** (1969) 925-946.