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Synthesis of rare-earth orthoaluminates by a polymer complex method

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Abstract

Rare-earth orthoaluminate was synthesized by a polymer complex method. The orthoaluminate compounds of La–Ho except for Ce and Pm were prepared in single phases, while those of Er–Lu were obtained only in mixed phases. The result indicated a tendency for a rare-earth element with larger sizes to take a perovskite structure as expected by tolerance factor.

Keywords: $LnAlO_3$; Phosphors; Chemical synthesis; X-ray diffraction

1. Introduction

The perovskite compounds with a chemical composition of ABX_3 are popular functional materials [1]. Especially, rare-earth orthoaluminate: $LnAlO_3$ (Ln: rare-earth element) is important for optical applications [2,3]. We found that a polymer complex method is useful for the synthesis of $LnAlO_3$ samples and succeeded in obtaining single-phase $YAlO_3$ for the first time [4]. The polymer complex method using a citric acid was invented by Pechini [5], and developed and reviewed by Kakihana et al. [6–8]. It is excellent in the stoichiometry kept strictly all through the synthesis in comparison with other solution techniques including a heterogeneous process. A stable chelate complex formed between a metal ion and citric acid is dispersed homogeneously in the polyester resin, and aggregation/segregation of metals in a subsequent heating process can be suppressed strongly due to the extremely small mobility of metals [6–8]. It is the reason why the target compounds with the homogeneous composition in atomic levels are obtained.

The polymer complex method has been applied to many kinds of samples, but there is no systematic study of $LnAlO_3$ series. In the present paper, we investigated the synthesis of the $LnAlO_3$ samples ($Ln = {}_{57}La–{}_{71}Lu$) by the polymer complex method, and discussed the results intensively in relation to their structures.

2. Experimental details

2.1. A synthesis process of $LnAlO_3$ by the polymer complex method

Flow chart for preparing $LnAlO_3$ by the polymer complex method is well known [6–8] and almost the same with that in our previous report [9]. Four starting materials of $Ln(NO_3)_3$ (Nippon Yttrium Co., Ltd., 99.9%), $Al(NO_3)_3$ (Kojundo Chemical Labolatory Co., Ltd., 99.9%), ethylene glycol ($C_2H_6O_2$, Wako Pure Chemical Industries Ltd., 99.5%) and citric acid ($C_6H_8O_7$, Wako Pure Chemical Industries Ltd., 98.0%) were mixed in the molar ratio of 1:1:40:10, respectively. The concentrations of Ln and Al solutions were determined by a chelatometric titration. The solution was stirred on a digital hot stirrer (AS ONE corporation, DP-1M) and heated at 80 °C until a gelation was occurred. The gelation usually terminated at the temperature of 85–110 °C. The yellowish gel obtained was put in a mullite crucible (AS ONE corporation) and charred at 300 °C for 2 h in an electric furnace (DENKEN Co., Ltd., KDF-S70). A black solid mass called a precursor was obtained. The precursor was then ground and heat-treated at 1150 °C for 2 h in a platinum crucible. Rare-earth elements used include ${}_{57}La$, ${}_{58}Ce$, ${}_{59}Pr$,

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$_{60}$Nd, $_{62}$Sm, $_{63}$Eu, $_{64}$Gd, $_{65}$Tb, $_{66}$Dy, $_{67}$Ho, $_{68}$Er, $_{69}$Tm, $_{70}$Yb, and $_{71}$Lu.

2.2. *Identification*

The polycrystalline sample obtained was identified by X-ray diffraction (XRD) technique (Mac Science Co., Ltd., MXP-3) under the conditions of Cu Kα radiation, the tube voltage of 40 kV and the tube current of 30 mA. The scanning speed and sampling width of XRD were 4°/min and 0.02°, respectively. A simulation by Rietveld program RIETAN-2000 [10] was used to identify extra peaks not shown in the International Center for Diffraction Data (ICDD) database.

3. Results and discussion

3.1. *The synthesis of LnAlO$_3$*

We tried to synthesize LnAlO$_3$ (Ln = $_{57}$La–$_{71}$Lu) by the polymer complex method in the synthetic quantity of 0.002 mol. The LnAlO$_3$ phase was obtained in a single phase for La, Pr, Nd, Sm, Eu, Gd, and Dy. As an example, the X-ray diffraction pattern of LaAlO$_3$ is shown in Fig. 1. The polycrystalline powder looks light pink. The pattern of Fig. 1A is in excellent agreement with that of rhombohedral LaAlO$_3$ (ICDD database 31-0022). The X-ray diffraction patterns of PrAlO$_3$, NdAlO$_3$, SmAlO$_3$, EuAlO$_3$, GdAlO$_3$, and DyAlO$_3$ also correspond to those in ICDD database, thus allowed to conclude that they are in single phases.

On the other hand, the samples of Er, Tm, Yb, and Lu were obtained in mixed phases. For example, the X-ray diffraction pattern of YbAlO$_3$ (white polycrystalline powder) shown in Fig. 2 was a mixed phase of the orthorhombic YbAlO$_3$ (ICDD database 24-1933), the cubic Yb$_3$Al$_5$O$_{12}$ (ICDD database 23-1476), and Yb$_2$O$_3$ (ICDD database 41-1106). Similarly, the samples for Tm and Lu were mixed phases with their own garnet compounds, while the sample for Er was a mixed phase with a small amount of Er$_2$O$_3$. The CeAlO$_3$ phase was not obtained at all, but almost CeO$_2$ single-phase was generated. It is considered to be due to the easy oxidation of Ce(III) to Ce(IV) during the heat treatment in air.

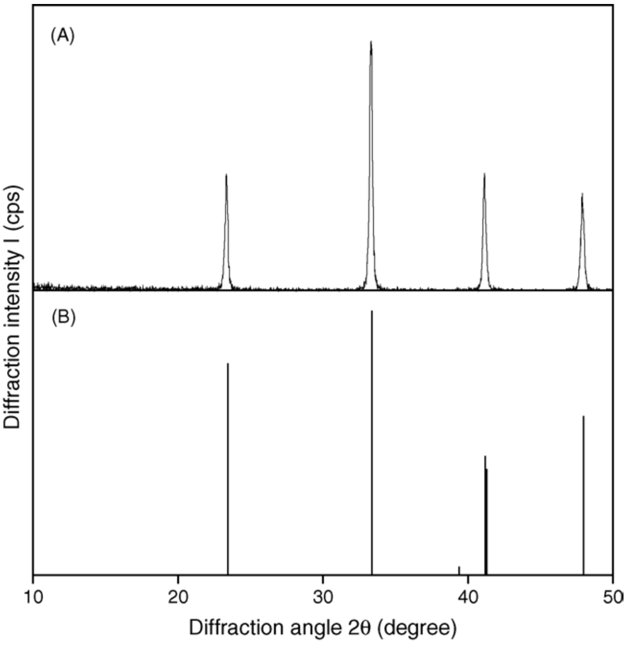

Fig. 1. X-ray diffraction patterns for the sample of LaAlO$_3$: (A) experimental and (B) database (rhombohedral, ICDD 31-0022).

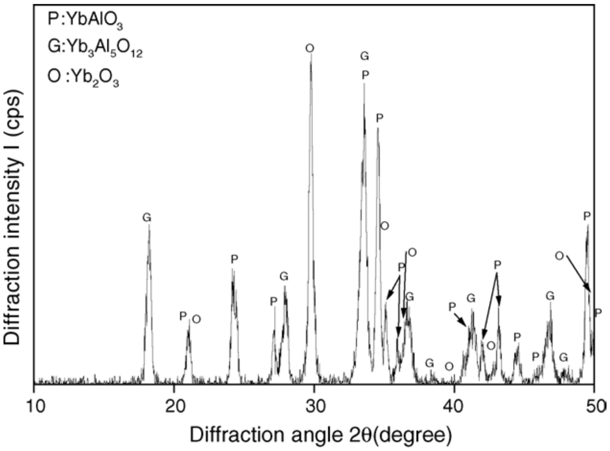

Fig. 2. X-ray diffraction pattern for the sample of YbAlO$_3$.

The X-ray diffraction patterns of TbAlO$_3$ and HoAlO$_3$ included few extra peaks not reported in the database. For example, the X-ray diffraction pattern of HoAlO$_3$ shown in

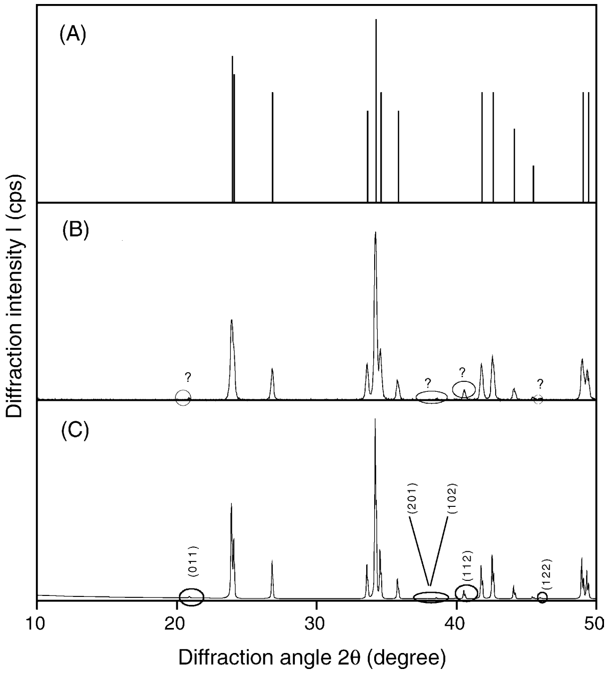

Fig. 3. X-ray diffraction patterns for the sample of HoAlO$_3$: (A) database (orthorhombic, ICDD 24-0470), (B) experimental, and (C) calculated.

Table 1
Result of synthesis

Element	Tolerance factor	Lattice parameters (Å)/crystal structure
$_{57}$La	0.8887	$a = 5.366$; $b = 5.366$; $c = 13.11$/rhombohedral
$_{58}$Ce	0.8807	–
$_{59}$Pr	0.8734	$a = 5.331$; $b = 5.331$; $c = 12.97$/rhombohedral
$_{60}$Nd	0.8708	$a = 5.320$; $b = 5.320$; $c = 12.92$/rhombohedral
$_{61}$Pm	0.8661	–
$_{62}$Sm	0.8617	$a = 5.285$; $b = 7.480$; $c = 5.284$/orthorhombic
$_{63}$Eu	0.8577	$a = 5.293$; $b = 7.452$; $c = 5.273$/orthorhombic
$_{64}$Gd	0.8544	$a = 5.302$; $b = 7.446$; $c = 5.254$/orthorhombic
$_{65}$Tb	0.8489	$a = 5.310$; $b = 7.419$; $c = 5.232$/orthorhombic
$_{66}$Dy	0.8449	$a = 5.317$; $b = 7.395$; $c = 5.209$/orthorhombic
$_{67}$Ho	0.8409	$a = 5.324$; $b = 7.374$; $c = 5.181$/orthorhombic
$_{68}$Er	0.8368	Orthorhombic (+$Er_3Al_5O_{12}$) + Er_2O_3
$_{69}$Tm	0.8332	Orthorhombic + $Tm_3Al_5O_{12}$ + Tm_2O_3
$_{70}$Yb	0.8288	Orthorhombic + $Yb_3Al_5O_{12}$ + Yb_2O_3
$_{71}$Lu	0.8262	Orthorhombic + $Lu_3Al_5O_{12}$ + Lu_2O_3

Fig. 3B contained extra peaks marked by a question mark than the basic pattern from a database (orthorhombic $HoAlO_3$, ICDD 24-0470). Since the XRD pattern of the synthesized sample is almost identical with that of orthorhombic $HoAlO_3$, it shows that $HoAlO_3$ was mainly synthesized. The extra peaks might be those of orthorhombic $HoAlO_3$. In fact, the calculation of reflection by using Rietveld simulation program RIETAN-2000 (Fig. 3C) is in good agreement with the observed one (Fig. 3B). The result for $TbAlO_3$ was almost the same. Therefore, we can conclude that both $TbAlO_3$ and $HoAlO_3$ were obtained in single phases, and that the database (ICDD 24-0470) for $HoAlO_3$ and the database (orthorhombic ICDD 24-1270) for $TbAlO_3$ are insufficient for small peaks.

3.2. *Perovskite structure and tolerance factor*

The results of $LnAlO_3$ synthesis by the polymer complex method are summarized in Table 1. A tolerance factor "*t*" is often used to estimate the stability of a perovskite structure, which is defined by the following formula [1]:

$$t = \frac{r_{\mathrm{Ln}} + r_{\mathrm{O}}}{\sqrt{2}(r_{\mathrm{Al}} + r_{\mathrm{O}})} \tag{1}$$

where r_{Ln}, r_{Al}, and r_{O} are ion radii of Ln^{3+}, Al^{3+}, and O^{2-}, respectively. The values of an ion radius by Shannon [11] were used. Perovskites with larger tolerance factors have rhombohedral phases, while those with smaller ones have orthorhombic phases. Further smaller ions seem to be difficult to form single phase of the perovskite. And the lattice parameters were determined by Rietveld analysis tentatively (goodness of fit [12] is less than 2). The lattice parameters *b* and *c* decrease in going from Sm to Ho, while the parameter *a* increases. This anomalous behavior of the parameter *a* was also reported for $LnFeO_3$ [13] and $LnGaO_3$ [14], which was attributed to the change of coordination number of rare-earth cations [15].

The result shows that the tolerance factor of 0.84 could be a boundary whether a single-phase $LnAlO_3$ is obtained or not. As mentioned above, $YAlO_3$ is difficult to get in a single phase. In fact, the ion radius of Y is 0.900 Å, located between Ho and Er, and the tolerance factor is 0.8405. Therefore, it is expected that this criterion will be useful for the $LnAlO_3$ synthesis by the polymer complex method.

4. Conclusions

We synthesized $LnAlO_3$ (Ln = $_{57}$La–$_{71}$Lu) by the polymer complex method. The $LnAlO_3$ samples of Ln = La–Ho except for Ce and Pm were obtained in a single phase, while those of Ln = Er–Lu were obtained only in mixed phases. It means that the rare-earth elements with a small ionic radius are difficult to form perovskite single phase as expected from the tolerance factor.

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