

## AN INVESTIGATION USING HIGH-PRESSURE SYNTHESIS OF DOUBLE-RARE-EARTH OXIDES OF $ABO_3$ -COMPOSITION

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The synthesis of the double-rare-earth oxides  $PrTmO_3$ ,  $PrYbO_3$ ,  $NdYbO_3$ ,  $NdLuO_3$ ,  $LaGdO_3$  and  $LaDyO_3$  is investigated by using high pressure and high temperature methods (4.0 GPa, 1200-1350°C) for the first time. The analyses by X-ray diffraction show that all products (except  $PrYbO_3$ ) are single-phase materials:  $NdLuO_3$  belongs to the P-type structure,  $PrYbO_3$  is mainly P-type, and the others belong to B-type. The  $PrTmO_3$  is a new material which has not yet been reported in the literature.

### 1. Introduction

The investigation of the structures and properties of the  $ABO_3$ -compositional compounds and solid solutions is one of the active research areas. At atmospheric conditions, the perovskite compounds  $LaR'O_3$  ( $R' = Ho-Lu, Y$ ),  $PrR'O_3$  ( $R' = Yb, Lu$ ) and  $NdLuO_3$  have been synthesized by Berndt et al. [1], but  $PrYbO_3$  and  $NdLuO_3$  have not been obtained in single-phase form. For the  $Nd_2O_3$ - $Yb_2O_3$  system, Coutures et al. [2] have indicated that at the equimolar constituent zone and above 1400°C it is a mixture of solid solutions  $B_{ss}$  and  $C_{ss}$ . Schneider et al. [3] and Muller-Buschbaum et al. [4] have predicted that for the  $La_2O_3$ - $Dy_2O_3$  and the  $Nd_2O_3$ - $Yb_2O_3$  systems the existence of perovskite-compound phases should be possible, but they did not make further study.

By using high pressure (at 20 kb, 1000°C after 1 h), Clark et al. [5] have prepared the pure perovskites  $AScO_3$  ( $A = Y, Dy-Tm$ ) which, under atmospheric pressure (at 1600°C after 60 h) were only obtained in the form of a two-phase mixture or C-type solid solution. From their results and from the work of the authors of the present paper [6] it can be seen that high pressure plays a very important role in the synthesis. In view of this,

some syntheses under high pressure for the  $ABO_3$ -compositional systems  $PrTmO_3$ ,  $PrYbO_3$ ,  $NdYbO_3$ ,  $NdLuO_3$ ,  $LaDyO_3$  and  $LaGdO_3$  have been studied in the present paper.

### 2. Experimental

The starting materials used had a purity of 99.9% or purer. They were weighed with an equimolar  $R_2O_3$ - $R'_2O_3$ , except for  $Pr_6O_{11}$ - $Tm_2O_3$  which was weighed according to 1/3:1. The treatment of the starting materials, the assembly, the calibration of pressure, the method of temperature measurement each time, the procedure to raise the pressure and temperature, and the analyses by using X-ray diffraction were the same as in ref. [6]. The values of the temperature, pressure and lattice parameters were correct to within  $\pm 30^\circ C$ ,  $\pm 1.5$  kb and  $\pm 0.004$  Å, respectively.

### 3. Results

The products, together with their synthetic conditions and structures and lattice parameters, are listed in table I. For each product diffractog-

Table I

Starting materials	Pressure (kb)	Temperature (°C)	Time (min)	Structure of products	Colour	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (deg)
$1/3\text{Pr}_6\text{O}_{11} + \text{Tm}_2\text{O}_3$	40	1350	30	Single-phase B	emerald green	14.212	3.572	8.782	100.75
	40	1250	30	Single-phase B	emerald green				
$1/3\text{Pr}_6\text{O}_{11} + \text{Yb}_2\text{O}_3$	40	1200	30	P, mainly		5.760	5.992	8.348	
	40	1100	30	P + A + B					
$\text{Nd}_2\text{O}_3 + \text{Yb}_2\text{O}_3$	45	1350	30	Single-phase, B	blue				
$\text{Nd}_2\text{O}_3 + \text{Lu}_2\text{O}_3$	40	1250	30	Single-phase, B	blue	14.114	3.545	8.729	100.80
	40	1200	30	Single-phase, P	blue	5.730	5.970	8.309	
$\text{La}_2\text{O}_3 + \text{Gd}_2\text{O}_3$	45	1350	30	Single-phase, B	White				
	40	1250	30	Single-phase, B	White	14.374	3.697	8.990	100.46
	30	850	30	B + A					
$\text{La}_2\text{O}_3 + \text{Dy}_2\text{O}_3$	40	1350	30	Single-phase, B	White	14.260	3.604	8.843	100.69
	40	1250	30	B + small A					
	40	950	30	B + A					
	29	1360	30	B	black	14.380	3.655	8.948	100.76

ram there are more than 30 peaks, which can be successfully indexed with the lattice parameters in table I. The products are well crystallized, for the peaks are sharp. For the  $\text{La}_2\text{O}_3 + \text{Dy}_2\text{O}_3$  system, the B-type structure of single phase is also obtained under 29 kb. However, the crystallinity is worse than that obtained under 40 kb, and its lattice parameters are larger.

#### 4. Discussion

(1) The B-type  $\text{PrTmO}_3$  and  $\text{NdYbO}_3$  and the P-type  $\text{NdLuO}_3$  were obtained in the form of single phase for the first time, but with the synthetic conditions of the present paper, the P-type  $\text{LaDyO}_3$  and  $\text{NdYbO}_3$  have not been prepared.

(2) The tolerance factor  $t$  is a useful empirical criterion for measuring the structural stability of the perovskite (e.g. P-type structure). In most cases the perovskite structure is stable with  $t$  lying between 0.8 and 0.9. By means of the values of the empirical ionic radii for an SP-76 [7] system, according to the radii of ions  $\text{A}^{3+}$  ( $=\text{La}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$ ) for 12-fold coordination (as there is no data for  $\text{Pr}_{12}^{3+}$ ,  $\text{Pr}_9^{3+}$  is used instead) and  $\text{B}^{3+}$  ( $=\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$ ,  $\text{Lu}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Dy}^{3+}$ ) for 6-fold coordination, the  $t$  calculated are 0.835

( $\text{NdLuO}_3$ ), 0.832( $\text{NdYbO}_3$ ), 0.807( $\text{PrLuO}_3$ ), 0.804 ( $\text{PrYbO}_3$ ), 0.800( $\text{PrTmO}_3$ ), 0.844( $\text{LaDyO}_3$ ), and 0.835( $\text{LaGdO}_3$ ). They are in the stable zone. Otherwise, the starting materials used in the present work were weighed and mixed equimolarly, and their structures were either A-type (hexagonal) or C-type (cubic), but the B-type products differ from A- and C-type structures. So the products can be looked upon as compounds of  $\text{ABO}_3$ -type perovskite with distortion forms of orthorhombic (e.g. P-type,  $\text{NdLuO}_3$  and  $\text{PrYbO}_3$ ) and monoclinic (e.g. structure B-type,  $\text{PrTmO}_3$ ,  $\text{NdYbO}_3$ ,  $\text{LaDyO}_3$  and  $\text{LaGdO}_3$ ) structure. It should be noticed, however, that the  $\text{R}'_2\text{O}_3$  ( $\text{R}' = \text{Gd}$ ,  $\text{Dy}$ ,  $\text{Tm}$ ,  $\text{Yb}$ ,  $\text{Lu}$ ) would transform into a B-type structure under 29 or 40 kb and 1200–1360°C [8], and the products are prepared from a high-temperature state quenched into room temperature by a cooling rate of 80–120°C/s under high pressure, so they may also be a B-type solid solution  $(\text{B}^{3+}, \text{A}^{3+})\text{O}_{1.5}$  of high temperature. For them it is necessary to further distinguish the difference between compound and solid solution.

It is worth indicating that, along with the increment of structural distortion (e.g. angle), the 12–6 coordination (e.g. space group Pbnm) of  $\text{A}^{3+}$  (with larger radius)- $\text{B}^{3+}$  (with smaller radius) will transform step by step into the 7-7 coordin-

ation (e.g. space group C2/m). Therefore, the products are similar to solid solutions and the disorder degree of ionic distribution is also increased. The mean cation radius  $\bar{r}$  for LaDyO<sub>3</sub> and LaGdO<sub>3</sub> is larger (equal to 1.035 Å and 1.050 Å, respectively) and in better accord with the structural stable condition [9] of B-type solid solution. For these reasons the products may also be looked upon as solid solutions.

(3) By comparing with the results obtained under atmospheric pressure, it can be seen that the high pressure also plays an important role like that of ref. [6]. That is to say, and high pressure can decrease the temperature of synthesis, accelerate the reaction rate, increase the transformation rate of products, and greatly shorten the synthetic time.

(4) After the products had been synthesized for 50 days, the X-ray diffractograms showed that there is no appreciable change in their structure. So the products are stable.

Moreover, it was found in the present work that the effect of the water and CO<sub>2</sub> contained in the La<sub>2</sub>O<sub>3</sub> is considerably important for the synth-

esis below 1350°C at 29–40 kb. They affect the structure of products.

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