

## Parameters Influencing on Mechanochemical Synthesis of Lanthanoid Ferrites

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Reactive grinding using a planetary ball-mill has been applied to the mechanochemical synthesis of lanthanoid ferrites,  $\text{LnFeO}_3$  (Ln: La, Pr, Sm, Gd, Dy, Yb). Colloidal lanthanoid hydroxides,  $\text{Ln}(\text{OH})_3$ , have first been formed from their oxides in organic liquids under grinding. The hydroxides not only promote the size reduction of the other reactant  $\text{Fe}_2\text{O}_3$  in acting as the grinding aid but react with  $\text{Fe}_2\text{O}_3$  to form hydroxide-complexes. The hydroxide complexes can be converted to  $\text{LnFeO}_3$  by the following stress-induced dehydration-condensation reaction. The reactivity strongly depends on the free energy change of hydroxide formation ( $\Delta G_R$ ) for the lanthanoid oxides and an electrostatic parameter of lanthanoid ions ( $Z/r$ ), where  $Z$  is the ionic charge number and  $r$  the ionic radius. Although the  $\Delta G_R$  values for all  $\text{Ln}_2\text{O}_3$  are negative, the high  $Z/r$  value disturbs the formation of hydroxide-complexes. The adequate combination of the starting materials and the influence of the grinding stress have been discussed.

Key words: Lanthanoid ferrite, synthesis, mixing-grinding, mechanochemistry, crystallization

### 1. INTRODUCTION

Refinement of reactant particles is particularly important for reactive grinding. It is efficiently attained by the use of soft matrices such as metals and inorganic salts, because of the effective absorption of the grinding stress due to their plastic deformation. It also makes the contact stress between reactant particles and soft matrices increase. McCormick *et. al.* describes the reactive grinding forming nano-size ceramics and metal particles with the size less than 10nm in reactive and deformable inorganic salts [1-2].

Colloidal materials are the alternatives to the reactive soft matrices. Most inorganic colloids, typically hydroxides, are agglomerated to form soft matrices in less-hydrophilic organic liquids by the repulsive force to the environmental liquids. The authors have applied the hydroxide colloids as the reactive matrices to the synthesis of  $\text{MTiO}_3$  [3],  $\text{MFe}_{12}\text{O}_{19}$  (M: Ba, Sr) [4],  $\text{Fe}_3\text{O}_4$  [5,6],  $\text{LaFeO}_3$  [7] and so on. Perovskite- $\text{LaFeO}_3$  is currently receiving significant attention as an intelligent catalyst support, where damaged catalyst particles can be repaired with the prevention to coarsening on it [8].  $\text{La}_2\text{O}_3$  was easily hydrated at the early stage of grinding to provide the reactive matrix and forms  $\text{LaFeO}_3$  via a hydroxide complex,  $\text{LaFeO}(\text{OH})_4$  [7]. The dehydration-condensation reaction forming  $\text{LaFeO}_3$  is a stress-induced reaction.

In the present paper, this reactive grinding process has been applied to the synthesis of a series of lanthanoid ferrites,  $\text{LnFeO}_3$  (Ln: La, Pr, Sm, Gd, Dy and Yb).

### 2. EXPERIMENTAL

High-purity lanthanoid oxide powders (purity: >99.9%) supplied from Hokko Chem. Ind. was used after the heat-treatment at 500°C for 3h. The specific surface area ( $SSA$ ) was 6.5 ( $\text{La}_2\text{O}_3$ ), 2.2 ( $\text{Pr}_6\text{O}_{11}$ ), 3.3 ( $\text{Sm}_2\text{O}_3$ ), 1.7 ( $\text{Gd}_2\text{O}_3$ ), 1.6 ( $\text{Dy}_2\text{O}_3$ ) and  $0.9 \text{ m}^2 \cdot \text{g}^{-1}$  ( $\text{Yb}_2\text{O}_3$ ). The starting  $\text{Fe}_2\text{O}_3$  was amorphous fine powder ( $SSA$ :  $207 \text{ m}^2 \cdot \text{g}^{-1}$ ) prepared by the calcination of  $\text{Fe}(\text{OH})_3$  at 200°C for 20h under vacuum. Mechanical grinding was conducted by the use of a planetary mill (Kurimoto-Tekko-Sho). The starting composition and the grinding condition are listed in Table 1. Weighed powders in the molar ratio of 1:1 (20g as  $\text{LnFeO}_3$ ) were encapsulated into the grinding vessel made of  $\text{Si}_3\text{N}_4$  (480 $\text{cm}^3$ , inner-diameter: 76mm) with acetone (75 $\text{cm}^3$ ), a small amount of distilled water and the grinding media ( $\phi 2\text{mm}$

Table I Condition for mixing-grinding operation

	Starting composition	Organic liquid media	Revolution speed, $f_{\text{rev}}$
LA6, LA5	$\text{Fe}_2\text{O}_3 + \text{La}_2\text{O}_3$	Acetone	6 s <sup>-1</sup> (3h)
PR6, PR5	$3\text{Fe}_2\text{O}_3 + \text{Pr}_6\text{O}_{11}$		
SM6, SM5	$\text{Fe}_2\text{O}_3 + \text{Sm}_2\text{O}_3$		
GD6	$\text{Fe}_2\text{O}_3 + \text{Gd}_2\text{O}_3$		5 s <sup>-1</sup> (5h)
DY6, DY5	$\text{Fe}_2\text{O}_3 + \text{Dy}_2\text{O}_3$		
YB6, YB5	$\text{Fe}_2\text{O}_3 + \text{Yb}_2\text{O}_3$		
LA6M	$\text{Fe}_2\text{O}_3 + 2\text{La}_2\text{O}_3 + 2\text{Fe}$	Acetone	6 s <sup>-1</sup> (3h)
PR6M	$3\text{Fe}_2\text{O}_3 + 2\text{Pr}_6\text{O}_{11} + 6\text{Fe}$	+H <sub>2</sub> O <sub>2</sub>	
PR6H	$\text{Fe}_2\text{O}_3 + 2\text{Pr}(\text{OH})_3$	Acetone	6 s <sup>-1</sup> (3h)
YB6H	$\text{Fe}_2\text{O}_3 + 2\text{Yb}(\text{OH})_3$		

Table II Parameters influencing on synthesis

	La <sub>2</sub> O <sub>3</sub>	Pr <sub>6</sub> O <sub>11</sub> (Pr <sub>2</sub> O <sub>3</sub> )	Sm <sub>2</sub> O <sub>3</sub>	Gd <sub>2</sub> O <sub>3</sub>	Dy <sub>2</sub> O <sub>3</sub>	Yb <sub>2</sub> O <sub>3</sub>	
$\Delta G_R / \text{kJ} \cdot \text{mol}^{-1}$	-75.55	-35.80	-65.15	-49.90	-50.80	-53.45	-43.85
Electrostatic parameter, $[Z/r] / \text{nm}^{-1}$	29	32	30	31	32	33	35

YTZ balls, fractional filling: 0.40). The water content ( $x$ ) was fixed to 4.00 in the form of  $\text{LnFeO}_3 \cdot x\text{H}_2\text{O}$ . Grinding treatment was performed for 3h with 15min cooling interval in every 1h grinding procedure to maintain the temperature below 50°C. After the treatment, the ground products were filtered with 0.2 $\mu\text{m}$  Teflon membrane, washed with acetone, and dried at 85°C for 16h under vacuum. The ground products were calcined at 300-700 and 1000°C for 30min in air for crystallization.

To reduce the  $\text{Pr}^{4+}$  ions in the starting  $\text{Pr}_6\text{O}_{11}$ , to  $\text{Pr}^{3+}$ , an Fe-doped composition PR6M (and LA6M as a reference) was examined, where  $\text{H}_2\text{O}_2$  is added to the grinding liquid in the stoichiometric requisition to oxidize the remained metallic iron to form  $\text{LnFeO}_3$ . The compositions PR6H and YB6H were examined so as to indicate the importance of hydroxide formation reaction in this process.

Crystalline phases of the ground products and calcined powders were identified by X-ray diffractometry (XRD,  $\text{CuK}\alpha_1$ , 40kV, 20mA). Morphology was observed by scanning electron microscopy (SEM, Hitachi, S4300). Dehydration behavior of the ground products was examined by TG-DTA (10  $\text{K} \cdot \text{min}^{-1}$ ). SSA was determined by a  $\text{N}_2$ -adsorption BET method.

### 3. RESULTS AND DISCUSSION

#### 3.1 Ground Products

Figure 1 shows the XRD profiles of the ground products. The contamination was less than 0.02%. The ground products were almost amorphous. But, XPS analysis of the ground products showed the

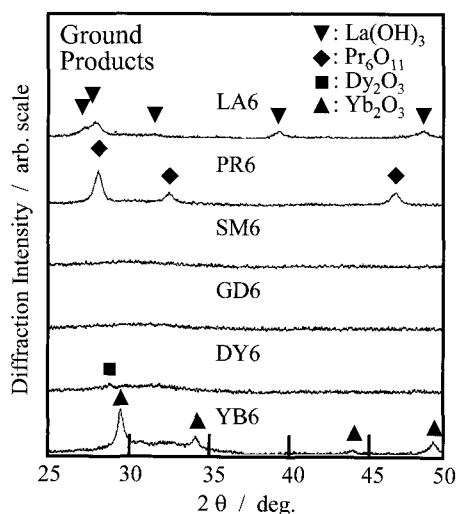
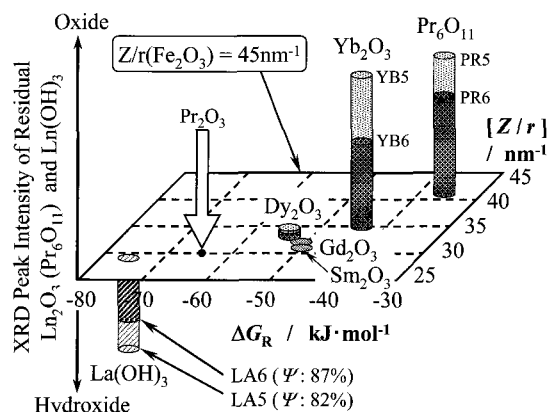


Fig. 1 XRD profiles of the ground products.

$\text{Ln-O-Fe}$  bond, meaning the formation of the rare-earth ferrites under grinding. However, the reaction was not completed and small amounts of the starting oxides (PR6, DY6, YB6) or the intermediate hydroxides (LA6) were crystallized after drying at 85°C. The reactivity of  $\text{Ln}_2\text{O}_3$  reduced with the increase in the atomic number of lanthanoid, that is the decreasing order of the ionic radius. Additionally, the reactivity of PR6 was irregularly poor.

In the previous work [8], the authors proposed a two-step reaction process for the formation of  $\text{LaFeO}_3$  [8]; the formation of hydroxide complex,  $\text{LnFeO}(\text{OH})_4$  and the dehydration-condensation of the complex. Table II shows the two parameters relating to the two reaction steps; Gibbs free energy change for hydration,  $\Delta G_R$ , and an electrostatic parameter,  $Z/r$ , indicating the ability of polarizing  $\text{OH}^-$  ions. When the difference in the  $Z/r$  values between lanthanoid ions and  $\text{Fe}^{3+}$  ( $Z/r=45 \text{ nm}^{-1}$ ) increases, the increased difference in the proton affinity results in the promotion of dehydration of the hydroxide complex. When plotting the XRD intensity of the residual oxide and hydroxide on a  $\Delta G_R - Z/r$  plane, Fig. 2 is obtained. It is evident that the excessively high  $\Delta G_R$  is the reason for the incomplete dehydration and the smaller negative values of  $\Delta G_R$  and the  $Z/r$  values close to that for  $\text{Fe}_2\text{O}_3$  results in the poor reactivity of  $\text{Yb}_2\text{O}_3$  and  $\text{Pr}_6\text{O}_{11}$ , although it is improved by the high grinding stress (compare the reactivity at  $f_{\text{rev}}=5$  to  $6 \text{ s}^{-1}$  in Fig. 2).

The  $Z/r$  value indicating the polarization ability to  $\text{OH}^-$  ions also influenced on the morphology of the ground products shown in Fig.3. The SSA decreased in the increasing order of the  $Z/r$  value;  $\text{LA6} > \text{SM6} > \text{GD6}$ . But the size of the agglomerates decreased in this order. This meant the hard agglomeration. The increase in SSA

Fig. 2 Influence of  $\Delta G_R$  and  $Z/r$  on reactivity under grinding.

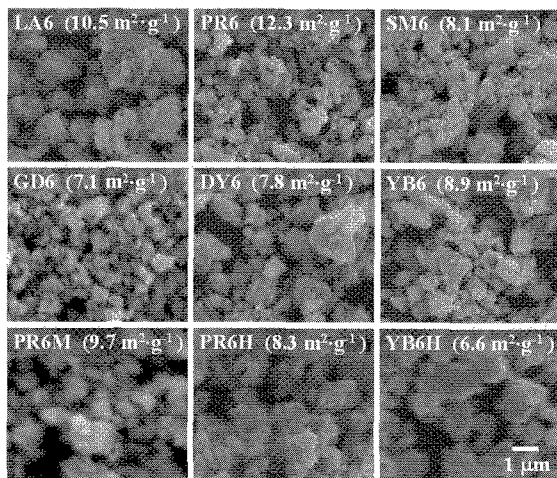


Fig. 3 Morphology of ground products, values brackets: SSA.

for DY6, YB6 and PR6 was due to the coexistence of the starting oxides.

### 3.2 Crystallization of the ground products

Figure 4 shows the temperature dependence of crystalline phases identified by XRD. The ground products crystallized to perovskite-LnFeO<sub>3</sub> without the re-crystallization to the starting oxides or the formation of any by-products. Then, the LnFeO<sub>3</sub> formed were stable compounds despite they were amorphous. The residual La(OH)<sub>3</sub> was consumed below 400°C and almost amorphous product formed at 400°C. Tetragonal perovskite was obtained above 500°C for LA6. The amorphous ground products SM6 and GD6 were directly crystallized to perovskite-LnFeO<sub>3</sub>, where the crystalline structure could be controlled from pseudo-tetragonal (500-600°C) to orthorhombic (>700°C). Remained Pr<sub>6</sub>O<sub>11</sub> in PR6 can be consumed accompanying with the crystallization to tetragonal phase at 500-600°C and then converted to orthorhombic phase above 700°C with the increase in crystallinity. DY6 and YB6 were crystallized directly to the orthorhombic phases. Tetragonal- and orthorhombic-LnFeO<sub>3</sub> with different crystallinity can be

prepared by using the amorphous ground products.

The crystallization temperature ( $T_C$ ) and the degree of hydration of the ground products ( $y$  in the form LnFeO<sub>3</sub>· $y$ H<sub>2</sub>O) determined by TG-DTA are plotted against  $Z/r$  in Fig. 5. The crystallization temperature increased with the decrease in  $Z/r$ . For PR5 and PR6,  $T_C$  was plotted on the curve for Ln<sup>3+</sup> ions rather than the position for the mixed ionic charge number  $Z=3.67$  for Pr<sub>6</sub>O<sub>11</sub>. Then, it was considered that almost Pr<sup>4+</sup> ions in the starting Pr<sub>6</sub>O<sub>11</sub> was reduced during grinding or the heat-treatment. The ground products were a little hydrated and showed a mass loss ranging from 7 to 10%. This corresponded to the  $y$  values of 1.3-0.7. The degree of hydration decreased with the increase in  $Z/r$ , agreed with the consideration on the dehydration ability due to the polarization of OH<sup>-</sup> ions. The extremely low  $y$  values for YB6 and PR6 was resulted from the coexistence of unreacted starting oxides.

### 3.3 Lattice parameters of crystallized LnFeO<sub>3</sub>

The orthorhombic lattice parameters ( $a_0$ ,  $b_0$ ,  $c_0$ ) and

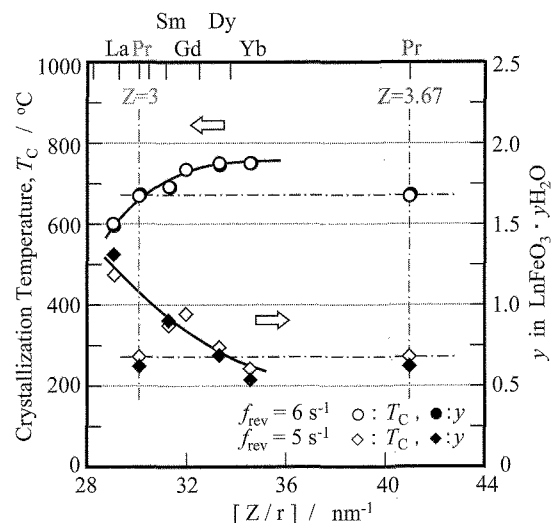


Fig. 5 Crystallization temperature and the degree of hydration.

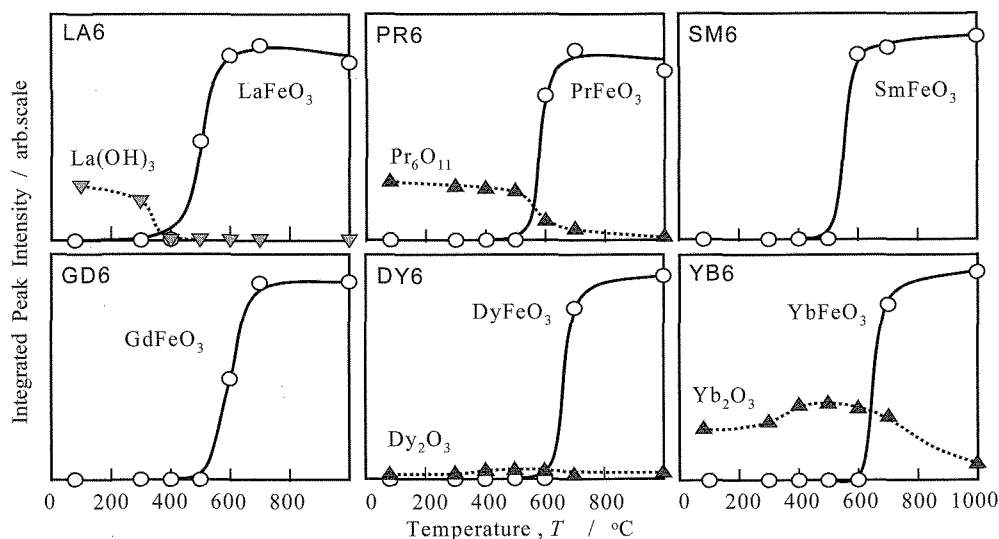


Fig. 4 Temperature dependence of crystalline phases.

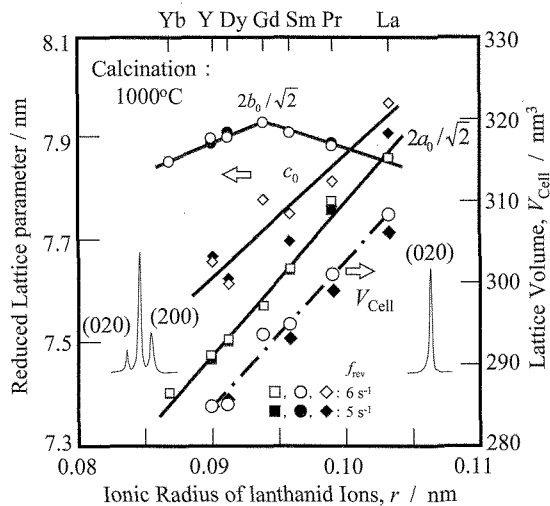


Fig. 6 Lattice parameters of  $\text{LnFeO}_3$  crystallized at  $1000^\circ\text{C}$ .

the lattice volume ( $V_C$ ) were plotted against the ionic radius ( $r$ ) of  $\text{Ln}^{3+}$  in Fig. 6. The lattice volume showed the almost linear relation to  $r$ . The lattice parameters for tetragonal- $\text{LaFeO}_3$  were very closed to each other. The lattice parameters  $a_0$  and  $c_0$  reduced in proportion to  $r$ . Contrary,  $b_0$  increased from  $\text{LaFeO}_3$  to  $\text{GdFeO}_3$  and then decreased. It was considered that this change in lattice parameters were related with the almost unchanged  $T_C$  for GD6, DY6 and YB6 in Fig. 5 and the gradually reducing stability of the intermediate tetragonal phases form  $\text{LaFeO}_3$  to  $\text{GdFeO}_3$ .

### 3.3 Improvement of the reactivity

It was considered that the poor reactivity of  $\text{Pr}_6\text{O}_{11}$  and  $\text{Yb}_2\text{O}_3$  was due to their less ability for hydration. However, the plot in Fig. 3 suggested that the reactivity of PR6 should be markedly improved to form amorphous- $\text{PrFeO}_3$  with a trace amount of intermediate  $\text{Pr}(\text{OH})_3$ , when  $\text{Pr}_6\text{O}_{11}$  was reduced to  $\text{Pr}_2\text{O}_3$ . The ground product PR6M shown in Fig. 7 proved this estimation. The metallic iron doped was completely consumed during grinding and did not crystallized to Fe or  $\text{Fe}_2\text{O}_3$  under the heat-treatment.

Another way to improve the reactivity was the use of hydroxides as the starting lanthanoid compounds. The

amorphous ground products PR6H and YB6H were directly crystallized to perovskite- $\text{LnFeO}_3$  without forming any other crystalline phases. The crystallization behavior through ( $\text{PrFeO}_3$ ) or without forming ( $\text{YbFeO}_3$ ) tetragonal phase agreed with that of PR6 and YB6. The use of metallic iron and hydroxides as the starting materials promoted the reactions under grinding markedly, however, the adhesion of metals and the huge amounts of OH groups on the reactant particles caused the unnecessarily high agglomeration as shown in Fig. 3. The SSA of PR6M, PR6H and YB6H became small. To synthesize the fine ground products, the addition of metallic iron and hydroxides should be limited to the minimum requirement.

### 4. CONCLUSION

Rare-earth ferrites,  $\text{LnFeO}_3$  (Ln: La, Pr, Sm, Gd, Dy and Yb), can be synthesized by a reactive grinding with the peculiarity of the stress-induced dehydration-condensation of the intermediate hydroxide complexes. The poor reactivity of  $\text{Pr}_6\text{O}_{11}$  and  $\text{Yb}_2\text{O}_3$  are improved by the use of reducing reagents and hydroxides.

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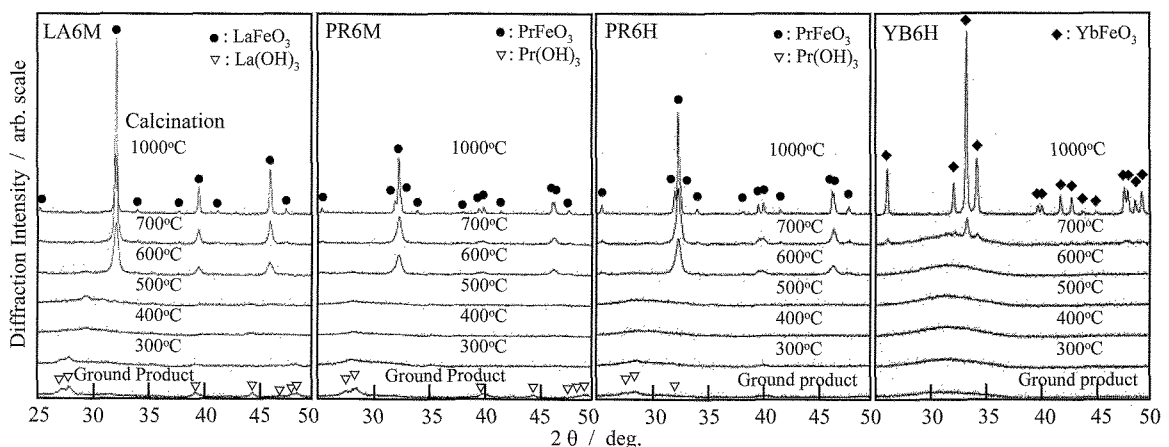


Fig. 7 Temperature dependence of crystalline phases for the ground products with metal-doping and hydroxide systems.