Synthesis of metastable rare-earth–iron mixed oxide with the hexagonal crystal structure

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ABSTRACT

Rare-earth–iron mixed oxides with the rare earth/iron ratio=1 have either orthorhombic (o-REFeO$_3$) or hexagonal (h-REFeO$_3$) structure. h-REFeO$_3$ is a metastable phase and the synthesis of h-REFeO$_3$ is usually difficult. In this work, the crystallization process of the precursors obtained by co-precipitation and Pechini methods was investigated in detail to synthesize h-REFeO$_3$. It was found that the crystallization from amorphous to hexagonal phase and the phase transition from hexagonal to orthorhombic phase occurred at a similar temperature range for rare earth elements with small ionic radii (Er–Lu, Y). For both co-precipitation and Pechini methods, single-phase h-REFeO$_3$ was obtained by shortening the heating time during calcination process. The hexagonal-to-orthorhombic phase transition took place by a nucleation growth mechanism and vermicular morphology of the thus-formed orthorhombic phase was observed. The hexagonal YbFeO$_3$ had higher catalytic activity for C$_3$H$_8$ combustion than orthorhombic YbFeO$_3$.

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1. Introduction

Orthorhombic rare-earth–iron mixed oxides (o-REFeO$_3$) having a perovskite structure with the space group of $Pbnm$ are thermodynamically stable for all the lanthanide elements and Y [1–4]. In this structure, Fe ions were surrounded by six oxide ions (FeO$_6$ octahedra). On the other hand, hexagonal REFeO$_3$ (h-REFeO$_3$) is known as a metastable phase. The space group of h-REFeO$_3$ has been reported to be $P6_3/mmc$ [5–7]. However, we have previously reported that the space group of h-REFeO$_3$ obtained by the glycothermal method is $P6_3cm$ [8], which is isomorphous with that of h-REMnO$_3$ (RE=Ho–Lu and Y) [8,9]. Other researchers have also reported the $P6_3cm$ space group for h-REFeO$_3$ [10,11]. In this structure, the transition metal ions are in unusual trigonal bipyramidal coordination surrounded by five oxygen atoms [8–11]. Although h-REMnO$_3$ also has the unique coordination structure of Mn, this phase is thermodynamically stable [12], and has been extensively studied for the multiferroic, magnetoresistance and sensor properties [13–15]. However, few studies on the application of h-REFeO$_3$ have been reported [5,16]. Although unique synthetic methods; i.e., the glycothermal method [9], thermal treatment of an amorphous phase obtained by hydrolysis of a yttrium–iron double alkoxide [6], quenching a melt (RE=Yb, Lu) [10,11], and spray-ICP technique [7] have been reported for h-REFeO$_3$, the synthesis of metastable h-REFeO$_3$ is difficult; thermodynamically stable o-REFeO$_3$ is preferentially formed by conventional methods such as solid state reaction or the co-precipitation method. So far as the authors know, synthesis of h-REFeO$_3$ by the co-precipitation method has never been reported.

In this work, the synthesis of h-REFeO$_3$ by conventional methods such as co-precipitation and Pechini methods was investigated. Correlation between the formation of hexagonal phase and ionic radii of rare earth elements was also investigated.

2. Experimental

2.1. Co-precipitation method

Iron nitrate nonahydrate (Fe(NO$_3$)$_3\cdot$9H$_2$O, 10 mmol) and rare earth nitrate hydrate (RE(NO$_3$)$_3\cdot n$H$_2$O, 10 mmol) were dissolved in 150 ml of water. To the solution, 50 ml of NH$_3$ solution containing 0.1 mol of NH$_3$ was added at once, and the suspension was stirred for 1 h. The product was washed with methanol by vigorous mixing and centrifuging, and dried in air at room temperature. The obtained precursor was calcined in air by heating at a rate of 10 °C/min to the prescribed temperature and holding at that temperature for 30 min unless otherwise mentioned. These samples were designated as CP(RE-xx) where xx is the calcination temperature in degree Celsius, and the as-synthesized samples were designated as CP(RE-as).

2.2. Pechini method

In 180 ml of water, 0.4 mol of citric acid was dissolved at 80 °C. Then, iron nitrate nonahydrate (Fe(NO$_3$)$_3\cdot$9H$_2$O, 10 mmol) and

rare earth carbonate hydrate ($RE_2(CO_3)_3 \cdot nH_2O$, 5 mmol) were added, and the mixture was magnetically stirred for 2 h at 80 °C to obtain a solution containing metal citrate complexes. To this solution, 0.4 mol of ethylene glycol was added, and the solution was stirred at 130 °C for 5 h to obtain a gelatinous solution. After the gel was heated in a mantle heater at 350 °C for 4–5 h, the thus-obtained brown powder was heated at the prescribed temperature at a rate of 10 °C/min and held at that temperature for 30 min unless otherwise mentioned. These samples were designated as PC(RE-xx) where xx is the calcination temperature in degree Celsius, and the as-synthesized samples were designated as PC(RE-as).

Catalyst tests for C_3H_8 combustion were performed in a fixed-bed reactor. The catalyst was tabletted, pulverized into 10–22 mesh, and set in the reactor. The reaction gas composed of 3000 ppm C_3H_8, 17% O_2, and He balance was introduced to the catalyst bed at $W/F = 0.3$ g s ml^{-1}. The effluent gases from the reactor were analyzed with a gas chromatograph (GC-8A, Porapak Q). The catalytic activity is expressed by the T_{50} value, which is defined as the temperature at which the catalyst exhibits 50% C_3H_8 conversion under the above-mentioned conditions.

X-ray powder diffraction (XRD: Model XD-D1, Shimadzu, Kyoto, Japan or Model Ultima IV, Rigaku, Tokyo, Japan) was performed using Cu $K\alpha$ radiation and a carbon monochromator. The morphology of products was observed with a transmission electron microscope (TEM: Model H-800, Hitachi, Tokyo, Japan). Simultaneous thermogravimetric and differential thermal analyses (TG–DTA, Model Thermo plus TG8120, Rigaku) were performed at a rate of 10 °C/min in a 50 ml/min flow of dried air.

3. Results and discussion

3.1. Syntheses of h-REFeO$_3$ by co-precipitation and Pechini methods

TG–DTA profiles of CP(RE-as) are shown in Fig. 1. A large weight loss was observed at 100–400 °C, which was associated with an endothermic peak due to the desorption of water adsorbed on CP(RE-as). An exothermic peak in DTA was observed at 600–800 °C without any weight loss.

The diffraction peaks due to h-REFeO$_3$ were clearly observed for CP(RE-800) for Y or Er–Lu. On the other hand, the products for La–Ho exhibited the diffraction peaks due to o-REFeO$_3$. These results indicate that the exothermic response at around 600–800 °C in DTA was due to the crystallization of hexagonal or orthorhombic phase from amorphous precursors.

For the sample obtained by the PC method, PC(RE-800) samples with the RE having small ionic sizes (Er–Lu and Y) were h-REFeO$_3$,

and PC(Ho-800) was a mixture of h-HoFeO$_3$ and o-HoFeO$_3$, while PC(RE-800) samples with larger RE elements (La–Dy) were o-REFeO$_3$. Except for the formation of the mixture of h-HoFeO$_3$ and o-HoFeO$_3$ in PC(Ho-800), the product spectrum of PC(RE-800) was essentially identical with that of CP(RE-800).

Fig. 2 shows the correlation between ionic radius and crystallization temperature of o-REFeO$_3$ and h-REFeO$_3$. The products for La, Nd and Sm were easily crystallized to the orthorhombic phase at low temperatures. For these products, the crystallization temperatures of the precursors obtained by the PC method were lower than those obtained by the CP method (Table 1).

In the case of the perovskite structure consisting of RE elements and iron, the tolerance factor, t, defined by Goldschmidt [17] becomes small with decreasing the ionic radius of the RE element [18,19], and the perovskite structure becomes less stable; therefore crystallization temperature of o-REFeO$_3$ drastically increased with decreasing the ion radius of the RE elements. As for REMnO$_3$, h-REMnO$_3$ is thermodynamically stable for the RE elements with small ionic sizes (Ho–Lu and Y) [12], while o-REMnO$_3$ is formed for
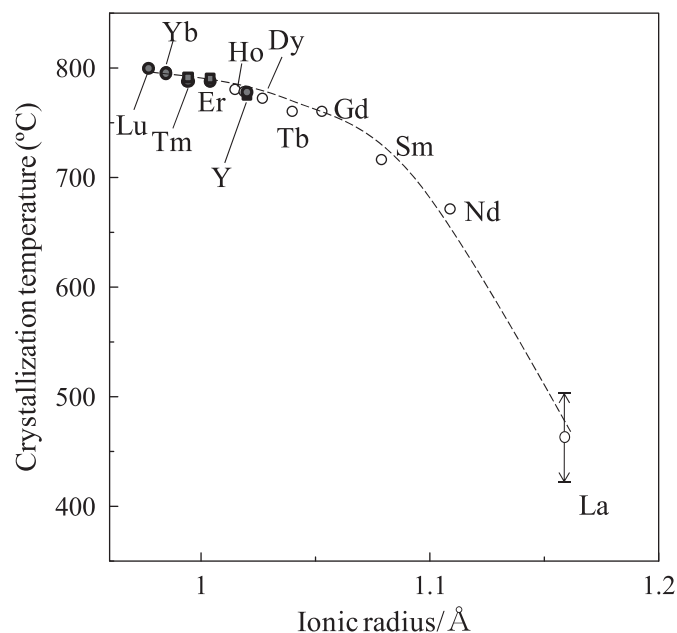
Fig. 2. Correlation between ionic radius and exothermic temperature observed by DTA of CP(RE-as) (circles) and PC(RE-as) (squares): open symbols show that o-REFeO$_3$ was obtained by calcination of CP(RE-as) at 800 °C for 30 min and closed symbols indicate the formation of h-REFeO$_3$.
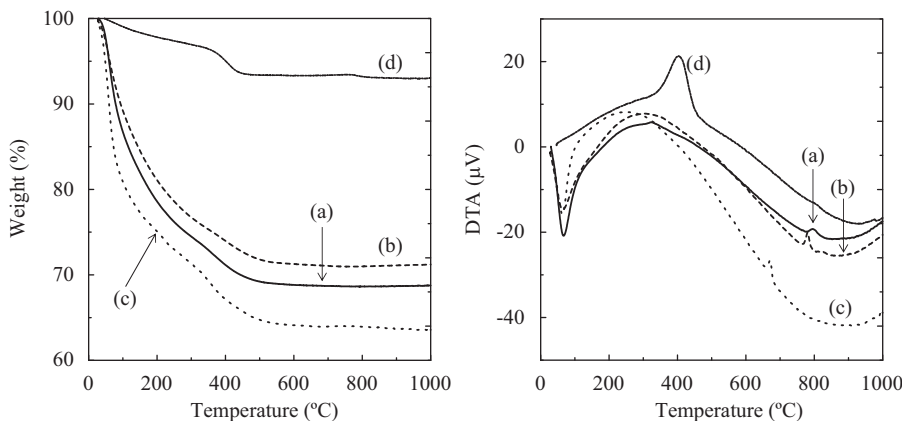
Fig. 1. TG–DTA profiles of: (a) CP(Yb-as); (b) CP(Ho-as); (c) CP(Nd-as); and (d) PC(Yb-as).