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New high-yield preparation procedure of $Ln[Fe(CN)_6]\cdot nH_2O$ (Ln = La, Gd, and Lu) and their thermal decomposition into perovskite-type oxides

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Abstract

The heteronuclear $Ln[Fe(CN)_6]\cdot nH_2O$ (Ln = La, Gd, and Lu) complexes were synthesized by the mixing of $(NH_4)_3[Fe(CN)_6]$ and $Ln(NO_3)_3$ methanol solutions as a new method. Their thermal decomposition products were then investigated. Although the yield of the $Ln[Fe(CN)_6]\cdot nH_2O$ complexes was ca. 20% for the well-known method in a water solution, it was improved to ca. 90% using this new method. The X-ray diffraction (XRD) patterns of the complexes agreed with those of the $Ln[Fe(CN)_6]\cdot nH_2O$ single phase for all the examined Ln systems. The $LnFeO_3$ single phase was obtained by the thermal decomposition of the synthesized heteronuclear complexes for Ln = La, Gd, and Lu.

Keywords: Chemical synthesis; X-ray diffraction; Thermal analysis

1. Introduction

Perovskite-type oxides are promising materials for many kinds of applications, such as chemical sensors, electrodes and electrolytes for fuel cells, and catalysts [1–3]. In general, polymetallic oxides have been prepared by the conventional solid reaction method. Chemical processing methods, such as the sol–gel method are used to obtain fine powders. As a new method, we proposed the thermal decomposition of heteronuclear complexes for the preparation of the di- or tri-metallic oxides. The heterometallic oxides with relatively high specific surface areas were formed at low temperatures, when the heteronuclear complexes were used as the precursors [4–10]. The decomposition of the heteronuclear $Ln[Fe(CN)_6]\cdot nH_2O$ (Ln = lanthanoid) hexacyano-complexes is a promising method for the preparation of homogeneous mixed oxides on an atomic level [11]. Up to now, the heteronuclear hexacyano-complexes have been prepared using the aqueous solutions mixture of $K_3[Fe(CN)_6]$ and the lanthanoid salt [11–14]. However, we have not obtained the heteronuclear complexes in high yield. We postulated that the yield of the complexes should improve, when a methanol solution is used instead of the water solution, since the solubility of the complex in methanol is lower than that in water. However, the usual $K_3[Fe(CN)_6]$ could not be used as a starting material because of its low solubility in methanol. From this point of view, we considered that the utilization of $(NH_4)_3[Fe(CN)_6]$ having a high solubility in methanol as the starting material would produce high yields of the $Ln[Fe(CN)_6]\cdot nH_2O$ complexes.

In this study, we prepared the $Ln[Fe(CN)_6]\cdot nH_2O$ (Ln = La, Gd, and Lu) complexes using $(NH_4)_3[Fe(CN)_6]$ with methanol. Their decomposition products were then stud-

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ied by thermogravimetry (TG) analysis and X-ray diffraction (XRD) to confirm the formation of the Ln:Fe = 1:1 complexes.

2. Experimental

We compared two sample preparation processes, i.e., for previous one (Method 1) and a new method (Method 2). For Method 1, the heteronuclear complex, $Ln[Fe(CN)_6]\cdot nH_2O$, was synthesized by mixing aqueous solutions of equimolar amounts of $K_3[Fe(CN)_6]$ (1.0 mol dm^{-3}) and $Ln(NO_3)_3\cdot nH_2O$ (1.0 mol dm^{-3}) under continuous stirring at room temperature. The resulting precipitate was collected by suction filtration and then washed with water, ethanol, and diethyl ether, before drying in air at 50 °C. For Method 2, the heteronuclear complex was synthesized by mixing 4:1 methanol solutions of equimolar amounts of $(NH_4)_3[Fe(CN)_6]$ (0.25 mol dm^{-3}) and $Ln(NO_3)_3\cdot nH_2O$ (1.0 mol dm^{-3}) under continuous stirring at room temperature for few min. The resulting precipitate was collected by suction filtration and then washed with ethanol and diethyl ether before drying in air at 50 °C. The $(NH_4)_3[Fe(CN)_6]$ as the starting material of Method 2 can be obtained by different routes: (1) the mixed solution of the $K_3[Fe(CN)_6]$ methanol suspension and NH_4Cl methanol solution (1:3 mol ratio) was separated into the KCl precipitate and the filtered solution; the filtered solution was concentrated to obtain the $(NH_4)_3[Fe(CN)_6]$ material and (2) the water suspension of $K_3[Fe(CN)_6]$ (1.0 mol dm^{-3}) and $(NH_4)_2C_2O_4$ powder (1:1.5 mol ratio) were mixed for 2 days, then separated into the $K_2C_2O_4$ precipitate and the filtered solution. The $(NH_4)_3[Fe(CN)_6]$ was obtained from the concentrated solution. In our case, we used method (2). In addition, we confirmed that $(NH_4)_3[Fe(CN)_6]$ was also obtained using the $La[Fe(CN)_6]\cdot 5H_2O$ complex (1.0 mol dm^{-3}) instead of $K_3[Fe(CN)_6]$ to form the $La_2(C_2O_4)_3$ precipitate.

The complex was decomposed at selected temperatures (in the range from 400 to 1000 °C) for 1 h, in order to obtain the perovskite-type powders. In order to characterize the complexes and the decomposition products, their X-ray diffraction patterns using Cu Kα radiation were recorded (Rint 2000, Rigaku, scanning rate = 2°/min at 40 kV and 20 mA). The thermal decomposition behavior was examined by TG analysis, performed at a heating rate of 5 °C/min in air.

3. Results and discussion

The $Ln[Fe(CN)_6]\cdot nH_2O$ complexes have been synthesized using our previous method (Method 1). The yield of the complexes was ca. 20% for all the Ln systems. With this method, it is very difficult to improve the yield using a highly concentrated solution, because the concentration of the $K_3[Fe(CN)_6]$ aqueous solution (1.0 mol dm^{-1}) as the starting material is almost at the maximum solubility limit.

Table 1
Yield of $Ln[Fe(CN)_6]\cdot nH_2O$ (Ln = La, Gd, and Lu) complexes using Method 2

Ln	*n*	Yield (%)
La	6	92
Gd	4	94
Lu	4	88

Hydrated *n* value was estimated using TG measurement.

Table 1 presents the yield of the complexes using the new method (Method 2). The yield was improved to ca. 90% for all the examined complexes. This high yield also suggests similar results for the other kinds of Ln-complexes. In this case, the *n* value in the complexes was estimated by the TG measurement. Fig. 1 shows the TG/DTA result of the $La[Fe(CN)_6]\cdot nH_2O$ complex. Dehydration by the loss of water of crystallization started at about 80 °C. A weight loss due to the exothermal decomposition of the ligand (confirmed by DTA) was confirmed at around 320 °C followed by a slower loss that ended at about 720 °C. The weight loss percentage of 51.5 wt% in the last plateau range gave ca. $n = 6$, which was greater than 55.0% for the general formula of the La-complex with five molecules of water tied up in the crystallization [12]. The complex and decomposed products were investigated by XRD are shown in Fig. 2. The XRD peak position for the complex agreed with that of $La[Fe(CN)_6]\cdot 5H_2O$, which has a hexagonal structure (space group: $P6_3/m$) [12]. In addition, the decomposed product at 400 and 500 °C showed the peaks of the $LaFeO_3$ phase with a "halo" at around 30 ° without those of the mono-metallic oxide phase, such as La_2O_3 and Fe_2O_3. The single perovskite phase was obtained at 600 °C or higher. This formation of the $LaFeO_3$ phase means that the synthesized material was pure $La[Fe(CN)_6]\cdot 5H_2O$ even for this high-yield method. The water absorption from atmosphere might be a cause for the

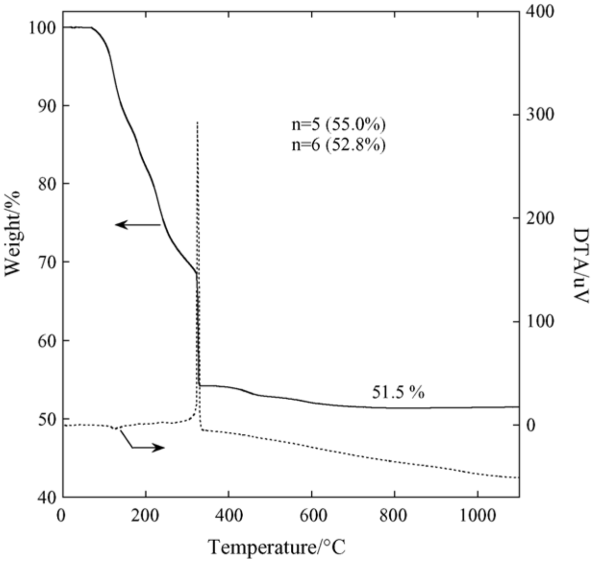

Fig. 1. TG/DTA result for $La[Fe(CN)_6]\cdot nH_2O$ complex (Method 2). Weights of experimental and (theoretical) of $n = 5$ and 6 are shown.

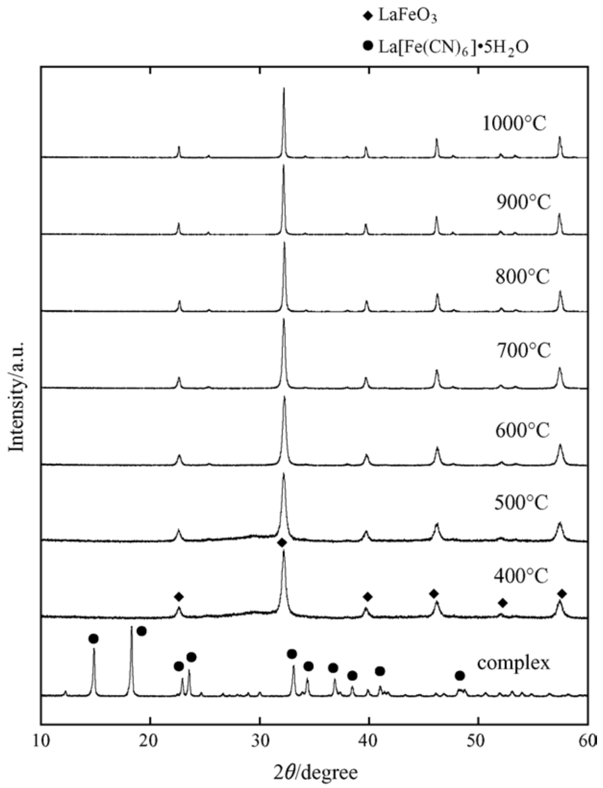

Fig. 2. XRD results of $La[Fe(CN)_6]\cdot nH_2O$ complex (Method 2) and decomposed products. Decomposed temperature is shown.

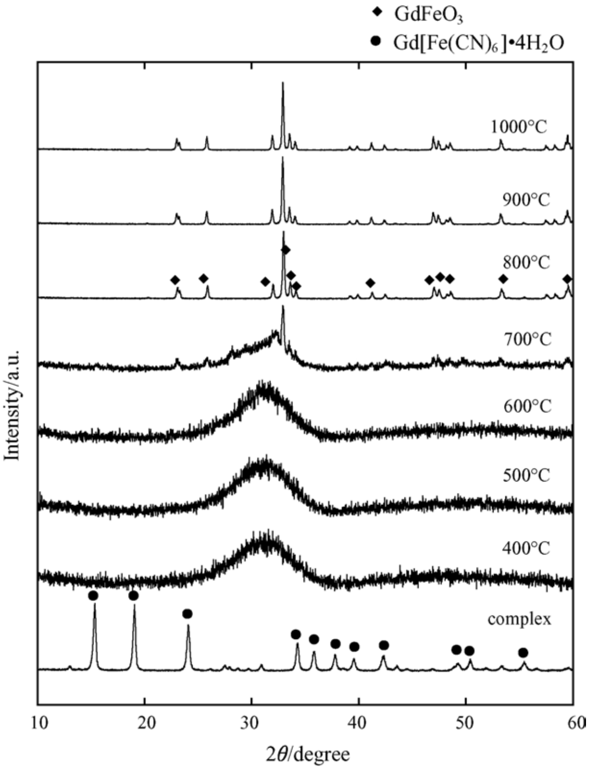

Fig. 3. XRD results of $Gd[Fe(CN)_6]\cdot nH_2O$ complex (Method 2) and decomposed products. Decomposed temperature is shown.

higher n value in the TG result for the LaFe-complex. It is confirmed that the full-width-at-half-maximum (FWHM) of all the $LaFeO_3$ peaks decreased with an increase in the decomposition temperature up to 1000 °C because of the crystallite growth.

For Ln = Gd and Lu, 58.5 and 60.1% for TG measurements of the decomposed materials almost agreed with the theoretical values of 59.1 and 60.6% as $n = 4$, respectively. Figs. 3 and 4 show the XRD results for the complex and decomposed products of Ln = Gd and Lu, respectively. The XRD peaks for each of the complexes showed an orthorhombic structure (space group: *CmCm*), which clearly agreed with the reported crystal having $n = 4$ [12]. For the decomposed products of Ln = Gd, the XRD patterns of the samples fired at 400–600 °C showed “halo” and no peaks. The peaks of the perovskite-type phase were detected from the samples decomposed at 700 °C. The $GdFeO_3$ single phase was obtained from the samples decomposed at or above 800 °C. In our previous paper, we reported that the single perovskite phase was formed by the thermal decomposition of the complexes for Ln = La, Pr, Nd, Sm, and Gd in the 600–900 °C in temperature range [4]. The temperature for the formation of the perovskite-type oxide gradually increased with an increase in the atomic number for Ln, i.e., a decrease in the ionic radius of the Ln^{3+} ion for Ln = La, Pr, Nd, Sm, and Gd. For the Ln = Gd system, the formation temperature (800 °C) of the single perovskite-type phase clearly agreed

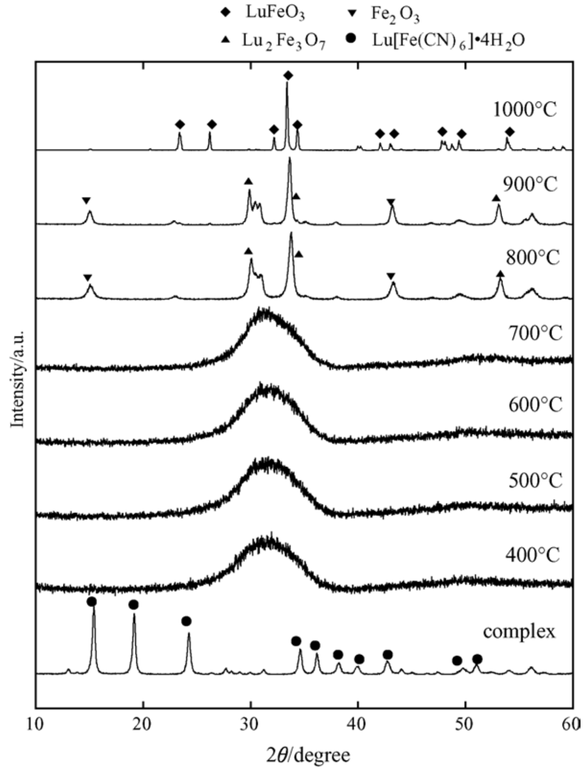

Fig. 4. XRD results of $Lu[Fe(CN)_6]\cdot nH_2O$ complex (Method 2) and decomposed products. Decomposed temperature is shown.

with that of our previous results [4]. The single phase of the perovskite-type oxide did not form for the heavy Ln = Dy and Ho of the decomposed samples even at 900 °C [4]. For Ln = Dy, the $DyFeO_3$ single phase was obtained by sintering at 1000 °C [1]. Up to now, the thermal decomposition products have not been investigated for the heavy Ln = Er, Tm, Yb, and Lu systems. Although the Lu^{3+} ion has the smallest ionic radius in the lanthanoid, the formation of the single perovskite $LuFeO_3$ phase was confirmed for the decomposed sample even at 1000 °C. From the XRD results for the complex and the decomposed material, it is very clear that the Ln:Fe ratio was 1:1 for all the samples synthesized by the new high-yield method (Method 2) using methanol.

4. Conclusions

The perovskite-type oxides are some of the most useful materials for many applications. We have been investigating the preparation of perovskite-type oxide powders having a high homogeneity and small particle size by the thermal decomposition of the appropriate hexacyano $Ln[M(CN)_6]\cdot nH_2O$ heteronuclear complexes. In this study, a new method was discovered for the high-yield (ca. 90%) preparation of the $Ln[Fe(CN)_6]\cdot nH_2O$ complexes by the mixing of $(NH_4)_3[Fe(CN)_6]$ and $Ln(NO_3)_3$ in methanol. This synthesis method is very useful for applications, such as chemical sensors and electrode materials for fuel cells.

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