Synthesis of \((\text{NH}_4)_2 x \text{La}_{1-x} \text{Sr}_x [\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}\) from two heteronuclear complexes \(\text{La}[\text{Fe}^{III}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\) and \((\text{NH}_4)_2 \text{Sr}[\text{Fe}^{II}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\) by mechanochemical process

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1. Introduction

Perovskite-type LnM03 heterometallic oxides (Ln = lanthanoid elements, \(M = \) tri-valent transition elements) have been studied extensively for their practical applications as catalysis,1–3/ electrode materials in fuel cells,4–6 and gas sensors.7,8 Many chemical processing methods have been widely adopted for the preparation of such perovskite-type oxides. On the other hand, it has been reported that the perovskite-type materials were synthesized by a mechanochemical reaction using a planetary ball-milling from Ln2O3 and M2O3 in air at room temperature.9,10 This method is almost identical to a mechanical alloying method for the preparation of an alloy phase from blended metals.11 One of the most superior preparation methods of the perovskite-type oxides having homogenous and fine particles is the thermal decomposition of the appropriate heteronuclear complexes containing a \(Ln:M = 1:1\) ratio from the hexacyano complexes such as \(\text{Ln}[\text{Fe}^{III}(\text{CN})_6] \cdot n\text{H}_2\text{O}\).12 In our previous study, the LnM03 and related perovskite-type materials have been prepared from the heteronuclear complexes such as hexacyano \(\text{Ln}[\text{M}^{III}(\text{CN})_6] \cdot n\text{H}_2\text{O}\) (\(M = \) Fe and Co).13,14 For the application of the electrode materials in fuel cells, the Sr2+ substituted perovskite-type materials of the Ln1–xSrxF03–α system have been utilized due to their high catalytic activity and electrical conductivity. However, the Sr containing heteronuclear hexacyanoferrate(II) complexes have not been reported, because the Sr2+ ions hardly substitute into the Ln3+ sites in the preparation process for the heteronuclear complex. As similar complexes, the thermal decomposition of \(\text{KLn}[\text{Fe}^{III}(\text{CN})_6] \cdot n\text{H}_2\text{O}\) (Ln = Lanthanide) has been reported by Goubard and Tabuteau.15,16 We synthesized a K free analogue \((\text{NH}_4)_2 \text{Ln}[\text{Fe}^{III}(\text{CN})_6] \cdot n\text{H}_2\text{O}\) complex and obtained its thermal decomposition products.17,18 For the alkali earth metal containing a hexacyano complex, Raistrick et al. reported the crystal structure of a \((\text{NH}_4)_2[M^{III}(\text{CN})_6]\) (\(M = \) Mg and Ca) complex.19 We briefly reported a single phase of a heteronuclear \((\text{NH}_4)_2 x \text{La}_{1-x} \text{Sr}_x [\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}\) complex synthesized by coprecipitation of two heteronuclear hexacyano complexes of \(\text{La}[\text{Fe}^{III}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\) and an analogous \((\text{NH}_4)_2 \text{Sr}[\text{Fe}^{III}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\).20 However, the mechanochemical reaction has not been reported between the large molecules of the heteronuclear complexes.

In this study, we succeeded in obtaining the \((\text{NH}_4)_2 x \text{La}_{1-x} \text{Sr}_x [\text{Fe}(\text{CN})_6] \cdot n\text{H}_2\text{O}\) heteronuclear complex by the mechanochemical reaction using a planetary ball-milling from two heteronuclear complexes of the synthesized \(\text{La}[\text{Fe}^{III}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\) and \((\text{NH}_4)_2 \text{Sr}[\text{Fe}^{III}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\). Furthermore, the perovskite \(\text{La}_{1-x} \text{Sr}_x \text{FeO}_3–\alpha\) oxide materials were prepared by the thermal decomposition at a low temperature.

2. Experimental

2.1 Chemical method in aqueous solution

The \(\text{La}[\text{Fe}^{III}(\text{CN})_6] \cdot 5\text{H}_2\text{O}\) heteronuclear complex was synthesized by mixing aqueous solutions of equimolar amounts of

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La(NO₃)₃·6H₂O and K₂Fe(CN)₆ with continuous stirring. The resulting precipitate was collected by suction filtration and washed with water, ethanol and diethyl ether, before drying in ambient air at room temperature. The complex, (NH₄)₂Sr[Fe(CN)₆] was almost quantitatively synthesized by mixing the equivalent amounts of Sr(NO₃)₂ (50 mmol in 20 ml water) and (NH₄)₂Fe(CN)₆·nH₂O (Wako Pure Chemical Industries, Ltd.) (ca. 14.4% H₂O content) (50 mmol in 20 ml water) under continuous stirring. After that, 400 ml of methyl alcohol was added to the mixed solution and then stirred for 1 h at 60–70°C. The resulting precipitate was collected by suction filtration and then washed with a small amount of water and methyl alcohol before drying in ambient air.

The (NH₄)₂xLa₁−xSrₓ[Fe(CN)₆]·nH₂O complex was synthesized by the coprecipitation of the two heteronuclear hexacyano complexes of La[Fe(III)₆(CN)₆]·5H₂O and (NH₄)₂Sr[Fe(II)₆(CN)₆]. Metal nitrates (10 mmol total) of (1−x)La(NO₃)₃·6H₂O and xSr(NO₃)₂ were dissolved in several ml of distilled water. In another beaker, the two iron hexacyano complexes (10 mmol total) of (1−x)K₂Fe(III)₆(CN)₆ and x(NH₄)₂Fe(II)₆(CN)₆·nH₂O (Wako Pure Chemical Industries, Ltd.) (ca. 14.4% H₂O content) were dissolved in 10 ml of distilled water. The two aqueous solutions were mixed for 2 h with continuous stirring. The resulting precipitate was collected by suction filtration and washed with a small amount of distilled water and methyl alcohol before drying in ambient air.

### 2.2 Mechanochemical method

Figure 1 shows a summary of the mechanochemical method. To synthesize the (NH₄)₂xLa₁−xSrₓ[Fe(CN)₆]·nH₂O complex using a ball-milling, two stoichiometric complexes (Total 0.01 mol = ca. 4 g) of (1−x)La[Fe(III)₆(CN)₆]·5H₂O and x(NH₄)₂Sr[Fe(II)₆(CN)₆] were wet ground (milling speed: ca. 300 rpm) by the LA-PO1 planetary ball mill of Itoh Co., Ltd. with a small amount (5 ml) of methanol for 24 h at room temperature, then dried at 60°C for a few hours. The ball-milling was also dry ground without methanol for 24 h. The ball-mill pot (inside diameter = 68 mm and inside height = 20 mm) and balls [diameter: 5 mm (50 balls) and 10 mm (10 balls)] were made of nylon and stabilized zirconia, respectively. The temperature of the samples after milling was around 30–40 and 40–50°C for the wet and dry processes, respectively.

### 2.3 Characterizations

The thermal decomposition process of the complex and the sintering processes were studied by thermogravimetric analysis (TG–DTA)(Seiko Instruments Inc.), performed at a heating rate of 10°C/min in dry air. The sample powder was dried at 50°C for 2 h in dry air before the TG–DTA measurement. X-ray diffraction (XRD, Model RINT 2200V, Rigaku Corporation, using a Cu-Kα radiation) analysis was used to investigate the structure of the thermal decomposition products. The elemental homogeneity of the samples was analyzed using SEM-EDX (Model JSM-6510LA, JEOL Corporation). The elemental ratio of La, Sr, and Fe was analyzed by an X-ray fluorescence analysis (XRF, Model RIX2100, Rigaku Corporation). Elemental analyses of H, C, and N in the precursors were carried out at the Central Elemental Analysis Laboratory, Faculty of Science, Kyushu University, Japan. The H, C, and N elemental contents of the complex were determined by measuring H₂O, CO₂, and NO₂ concentrations in the gas formed from the decomposition of the complex at elevated temperatures.

### 3. Results and discussion

#### 3.1 (NH₄)₂xLa₁−xSrₓ[Fe(CN)₆]·nH₂O heteronuclear complexes

Figure 2 shows the XRD results for the synthesized (NH₄)₂xLa₁−xSrₓ[Fe(CN)₆]·nH₂O heteronuclear complexes. The crystal structure of the (NH₄)₂Sr[Fe(II)₆(CN)₆] complex (X = 1.0) complex was estimated to be a tetragonal phase. The crystal structure of La[Fe(III)₆(CN)₆]·5H₂O (X = 0) complex is a hexagonal unit cell (space group: P6₃/m). In this hexagonal structure, the La⁺⁺ sites in La[Fe(III)₆(CN)₆]·5H₂O were coordinated by six nitrogens and three oxygens (9 C.N.). For the Sr-contained samples, the peak position shifted to a small d-spacing. The lattice constants decreased due to the difference in the N-O and La-O distance with the change in the La−N−C angle as reported for the KLa[Fe(III)₆(CN)₆]·4H₂O complex. Furthermore, the peaks of the (NH₄)₂Sr[Fe(II)₆(CN)₆] complex completely disappeared in the XRD pattern. These results prove that the reaction of two complexes did occur to form the single La−Sr−Fe heteronuclear complex. The X values of the starting materials and the analyzed X values using XRF for the (NH₄)₂xLa₁−xSrₓ[Fe(CN)₆]·nH₂O complex were also shown in Fig. 2. The analyzed X value was estimated based on the elemental ratio of Sr and La using XRF. The X values of the starting materials of 0.5, 0.6, 0.7, 0.8, 0.9 and analyzed X values using XRF are also shown in the figure.

![Fig. 1. (Color online) Summary of mechanochemical method.](image-url)
decreased to 0.06, 0.20, 0.26, 0.28, 0.39 due to the formation of the heteronuclear complex, respectively, because the complexation ability of the Sr$^{2+}$ ion would be lower than that of the La$^{3+}$ ion in the hexacyano iron complex.

### 3.2 Mechanochanical reaction

**Figure 3** shows the XRD results for the ball-milled powder using a wet process between the (1 $- X$)La[Fe$^{III}$(CN)$_6$]$\cdot$5H$_2$O and X(NH$_4$)$_2$Sr[Fe$^{II}$(CN)$_6$]. For the La[Fe$^{III}$(CN)$_6$]$\cdot$5H$_2$O ($X = 0$) and (NH$_4$)$_2$Sr[Fe$^{II}$(CN)$_6$] ($X = 1$) samples, the peak position did not change after ball-milling. The XRD pattern for $X = 0.4$ was almost agreed with peaks of (NH$_4$)$_2X$La$_{1-X}$Sr$X$[Fe(CN)$_6$]$\cdot$nH$_2$O heteronuclear complexes in Fig. 2. For $X = 0.2$, the peaks showed the mixture of two complexes. The peaks of the (NH$_4$)$_2$Sr[Fe$^{II}$(CN)$_6$] complex appeared for $X = 0.5$ and its intensity was increased with an increase in the X value. At first, we considered this reaction between two complexes processed via solvent. The single phase for $X = 0.4$ was also obtained by the reaction of the two complexes using water and an ethanol solvent. **Figure 4** shows the XRD peaks for complexes of chemical method ($X = 0.39$), the mechanochemical method ($X = 0.40$) with methanol and without solvent (dry process), and $X = 0$. From these results, the chemical formula for the reacted complex of $X = 0.4$ of the 0.6La[Fe$^{III}$(CN)$_6$]$\cdot$5H$_2$O and 0.4(NH$_4$)$_2$Sr[Fe$^{II}$(CN)$_6$] seems to be (NH$_4$)$_2X$La$_{0.6}$Sr$_{0.4}$[Fe(CN)$_6$]$\cdot$4.2H$_2$O whose 4.2H$_2$O and 0.8NH$_4$ were occupied in 5 hydration sites in the hexagonal complex. Although the total H$_2$O content is larger than that of the starting complexes for this reacted X = 0.4 complex, the moisture in ambient air or methanol solvent in the ball-mill pot may be reacted with the complexes. In the case of $X > 0.4$, the mixed products would be the mixture of two complexes for (NH$_4$)$_2X$La$_{0.6}$Sr$_{0.4}$[Fe(CN)$_6$]$\cdot$4.2H$_2$O and X(NH$_4$)$_2$Sr[Fe$^{II}$(CN)$_6$]. To clarify the formation of hexagonal complex, an elemental analysis was performed for the samples of $X = 0.4$.

**Table 1.** Elemental contents in the samples. The calculated values are shown in ( ) in this table

| X   | 0  | 0.2 | 0.4 | 0.5 | 0.6 | 0.8 | 1.0 |
|-----|----|-----|-----|-----|-----|-----|-----|
| H (%) | 2.35 (2.29) | 2.55 (2.53) | 2.71 (2.78) | 2.77 (2.73) | 3.00 (2.67) | 2.57 (2.55) | 2.49 (2.40) |
| C (%) | 16.84 (16.34) | 17.28 (16.73) | 17.47 (17.14) | 17.82 (17.74) | 20.11 (18.38) | 19.47 (19.80) | 21.03 (21.47) |
| N (%) | 18.77 (19.06) | 20.47 (19.74) | 22.34 (22.66) | 23.65 (24.13) | 24.75 (25.72) | 28.52 (29.25) | 32.48 (33.39) |

**Figure 5.** (Color online) Hydration n value for (NH$_4$)$_2X$La$_{0.6}$Sr$_{0.4}$[Fe(CN)$_6$]$\cdot$nH$_2$O.
mechanochemical reaction. This means the two complexes was reacted to form the single phase of the hexagonal (NH₄)₀.₈-La₀.₆Sr₀.₄[Fe(CN)₆]·₄.₂H₂O for X₀.₄.

**Figure 6** shows the SEM-EDX results for the ball-milled \(X₀.₄\) complex sample using wet process. The sample was pressed to obtain a flat surface. Elemental analyses were performed on the same surface observed by SEM [Fig. 6(a)]. The bright part of the elemental maps (b) (c) (d) means relatively high in elemental concentration. The elemental distribution of La (b), Sr (c), and Fe (d) was homogeneous for the complex. The La\(^{3+}\) ions would be substituted by Sr\(^{2+}\) ion as a similar concentration in the complex. In the case of \(X₀.₅\) (Fig. 7), the Sr element from (NH₄)₂Sr[Fe\(^{II}\)(CN)₆] complex as shown the XRD result was heterogeneously distributed on the surface for \(X₀.₅\) complex.

For the other combinations of the complexes in the mechanochemical reaction, we examined the differences between the (NH₄)La[Fe\(^{II}\)(CN)₆]·nH₂O and (NH₄)²Sr[Fe\(^{II}\)(CN)₆] complexes, and between (NH₄)La[Fe\(^{II}\)(CN)₆]·4H₂O and La[Fe\(^{III}\)(CN)₆]·5H₂O. However, these combinations of complexes did not react at all. This means that the reaction of La[Fe\(^{III}\)(CN)₆]·5H₂O and (NH₄)²Sr[Fe\(^{II}\)(CN)₆] is a very peculiar case. The hydrated H₂O in the LaFe\(^{III}\) and NH₄\(^{+}\) ion in SrFe\(^{II}\) complexes was replaced with the replacements of Sr\(^{2+}\) ion to La\(^{3+}\) sites with the physical contacts between two complexes. The mechanism for the mechanochemical reaction is not clear at present.

3.3 Thermal decomposition products
**Figure 8** shows the TG-DTA results of the ball-milled powder for the \(X₀.₄\) sample. Thermal decomposition was gradually proceeded below ca. 250°C. Further heating caused an abrupt weight loss around 280°C with a strong exothermal peak in the DTA result due to the decomposition of the cyanide groups, and two plateaus appeared around 300 and 530°C. The final plateau was observed from 620°C and higher temperatures and the weight loss percentages in this plateau were 51.9% which is in agreement with that (52.0%) calculation assuming the formation of La₀.₆Sr₀.₄FeO₂.₈ from the estimated (NH₄)₀.₈La₀.₆Sr₀.₄-[Fe(CN)₆]·₄.₂H₂O (\(X₀.₄\)).

**Figure 9** shows the XRD peaks of the thermal decomposition products at various temperature for 1 h in ambient air for \(X₀.₄\) complex. The decomposition temperatures in °C are shown in the figure.
(FWHM) of all the peaks decreases with an increase in the decomposition temperature because of the crystallite growth. The lattice constant was $a = 0.5525 \text{ nm}$, $b = 7806 \text{ nm}$, and $c = 0.5509 \text{ nm}$, for $X = 0.4$ which was smaller than $a = 0.5560 \text{ nm}$, $b = 7860$, and $0.5552 \text{ nm}$ for $X = 0$ (LaFeO$_3$). The ionic radius of Sr$^{2+}$ ion (0.126 nm) for 8 coordination number (8 CN) is larger than that of La$^{3+}$ ion (0.116 nm). The increase in Fe$^{4+}$ ion content and oxygen defect concentration introduced by the substitution of Sr$^{2+}$ is attributed to the decrease in lattice parameters. The ionic radius of Fe$^{4+}$ ion (0.0585 nm for 6 CN) is smaller than that of Fe$^{3+}$ ion (0.0645 nm).

4. Conclusions

It was found that the mechanochemical reaction using the physical ball-milling between two hetetonuclear complexes of $(1 - X)$La[Fe$^{III}$(CN)$_6$].5H$_2$O and X(NH$_4$)$_2$Sr[Fe$^{II}$(CN)$_6$] was possible to form a new La–Sr–Fe complex. This method can expect to synthesize new homogeneous hetetonuclear complexes having a focused elemental ratio, because the reaction of the materials processes in a closed ball-mill pod without filtration. We are going to clarify the combination of complexes and its mechanism for the mechanochemical reaction in the future.

References

1) J. G. McCarty and H. Wise, Catal. Today, 8, 231–248 (1990).
2) C. Tealdi, M. S. Islam, C. A. J. Fisher, L. Malavasi and G. Flor, Prog. Solid State Chem., 35, 491–499 (2007).
3) M. Asamoto, N. Harada, Y. Iwamoto, H. Yamamura, Y. Sadaoka and H. Yahiro, Top. Catal., 52, 823–827 (2009).
4) N. Q. Minh, J. Am. Ceram. Soc., 76, 563–588 (1993).
5) F. L-Joud, G. Gauthier and J. Mougin, J. Appl. Electrochem., 39, 535–543 (2009).
6) E. V. Tsipis and V. V. Kharton, J. Solid State Electrochem., 2, 1367–1391 (2008).
7) H. Aono, M. Sato, E. Traversa, M. Sakamoto and Y. Sadaoka, J. Am. Ceram. Soc., 84, 341–347 (2001).
8) H. Aono, E. Traversa, M. Sakamoto and Y. Sadaoka, Sens. Actuators, B, 89, 132–139 (2003).
9) Q. Zhang, J. Lu and F. Saito, Powder Technol., 122, 145–149 (2002).
10) Q. Zhang and F. Saito, J. Alloys Compd., 297, 99–103 (2000).
11) C. Suryanarayana, Prog. Mater. Sci., 46, 1–184 (2001).
12) P. K. Gallagher, Mater. Res. Bull., 3, 225–232 (1968).
13) Y. Sadaoka, K. Watanabe, Y. Sakai and M. Sakamoto, J. Alloys Compd., 224, 194–198 (1995).
14) Y. Sadaoka, H. Aono, E. Traversa and M. Sakamoto, J. Alloys Compd., 278, 135–141 (1998).
15) F. Goubard and A. Tabuteau, J. Solid State Chem., 167, 34–40 (2002).
16) F. Goubard and A. Tabuteau, Synthesis, Spectroscopic, 14, 257–262 (2003).
17) K. Sato, S. Itoh, K. Yamaguchi, M. Kurihara, M. Sakamoto, H. Aono and Y. Sadaoka, J. Ceram. Soc. Japan, 118, 384–386 (2010).
18) H. Aono, T. Nishida, M. Kurihara, M. Sakamoto and Y. Sadaoka, Ceram. Int., 38, 2333–2338 (2012).
19) I. D. Raistrick, N. Endow, S. Lewkowitz and R. A. Huggins, J. Inorg. Nucl. Chem., 39, 1779–1783 (1977).
20) H. Aono, T. Nishida, T. Kan, Y. Jin-oka, M. Kurihara, M. Sakamoto and Y. Sadaoka, Mater. Lett., 83, 151–153 (2012).
21) F. Hulliger, M. Landolt and H. Vetsch, J. Solid State Chem., 18, 283–291 (1976).
22) G. W. Beall, D. F. Mullica and W. O. Milligan, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 34, 1446–1449 (1978).
23) R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 32, 751–767 (1976).
24) J. Mizusaki, M. Okayasu, S. Yamauchi and K. Fueki, J. Solid State Chem., 99, 166–172 (1992).
25) K. Iwasaki, T. Ito, M. Yoshino, T. Matsui, T. Nagasaki and Y. Arita, J. Alloys Compd., 430, 297–301 (2007).