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Preparation of Perovskite-type $LaFeO_3$ by Thermal Decomposition of Heteronuclear Complex, $\{La[Fe(CN)_6]\cdot 5H_2O\}_x$

Susumu NAKAYAMA,[†] * Masatomi SAKAMOTO,* Kimihiro MATSUKI, Yoshihisa OKIMURA, Rie OHSUMI, Yusuke NAKAYAMA, and Yoshihiko SADAOKA*

[†] New Materials Research Center, Shinagawa Refractories Co.LTD., Inbe, Bizen 704

Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama 790

Submicron perovskite-type, $LaFeO_3$, powders were prepared by the thermal decomposition of a title cyanide-bridged heteronuclear complex. The decomposition begins at about 50 °C and the formation of $LaFeO_3$ proceeds above 580 °C. Mean particle diameter and specific surface area were 50 nm and 22.7 m^2/g, respectively, for the $LaFeO_3$ obtained by calcining at 620 °C.

It is well known that the finer perovskite-type oxides are the interesting mixed oxides, which exhibit characteristics (highly nonstoichiometry and mixed conductivity by both ionic and electronic charge carriers) relevant to functional materials such as electrical semiconductor for gas sensor with high sensitivity, catalysts for complete oxidation of hydrocarbons, and semipermeability of oxygen. As a conventional method, the solid state reactions of oxides, oxalates or carbonates of metal components above 1000 °C have been applied for the preparation of perovskite-type oxides. However, there are some problems in such method: First, it is difficult to prepare the finer powder of homogeneous oxide because of solid-state reaction. Second, repeated grinding and firing at a higher temperature is neccesary to eliminate the unreacted material. Third, the high-temperature treatment makes it difficult to prepare the perovskite which has a high surface area. In order to overcome these inevitable disadvantages, to lower the reaction temperature, and to prepare finer and homogeneous powders with high specific surface area, the developments of new preparation techniques, which include sol-gel technique, are of recent interest.[1)] Among of them, Yamazoe et al.[1d)] reported a noteworthy result that some perovskite-type oxides with high specific surface areas can be prepared at relatively low temperature by adding an excess of citric acid to an aqueous solution of metal nitrates. Recently, we proposed a new method which is based on the thermal decomposition of heteronuclear complexes isolated in advance, and found that the perovskite-type oxide with relatively high specific surface area was formed even at low temperature when $[Co(NH_3)_6][La(CO_3)] \cdot H_2O$,[2] $La[Cr(CH_2(COO)_2)_3] \cdot 6H_2O$,[3] and $\{Ln[Cr(C_2O_4)_3] \cdot 10H_2O\}_x$ (Ln=La, Pr, or Nd)[4] were used as starting complexes. Such decomposition of heteronuclear complexes is a promising method for the preparation of homogeneous perovskites in an atomic level with high specific surface area, if it is possible to isolate the easily decomposable complexes. From this point of view, in the present work we investigated the thermal decomposition behavior of the title complex and the $LaFeO_3$ obtained was characterized. The complex, $La[Fe(CN)_6] \cdot 5H_2O$ (reddish orange powder), was synthesized by mixing the equivalent amounts of lathanum(III) nitrate hydrate and potassium hexacyanoferrate(III) under stirring in water.[5] The IR spectrum of complex shows the ν(CN) stretching vibrations at 2140 and 2065 cm^{-1}, whereas the corresponding vibrations for $K_3[Fe(CN)_6]$ are observed at 2120 and 2045 cm^{-1}. These shifts to higher frequencies indicate the coordination of nitrogen to La(III)[6] and the construction of the three-dimensional network structure by Fe(III)-CN-La(III) linkage as reported by Bailey et al.[7]

Figure 1 shows the TG curve of the complex with the heating rate of 5 °C/min in ambient air. The decomposition begins at about 50 °C and the plateau is observed in the temperature range of 250 to 300 °C. The weight loss percentage at 280 °C is about 20%, which is in good agreement with the value (20.43%) calculated by assuming the formation of anhydrate. Further heating causes an abrupt weight loss by the decomposition of cyanide group, and plateaus are slightly observed in the ranges of 320 to 370 °C and 460 to 540 °C, followed by the last plateau above 580 °C. The weight loss percentage (44.29%) in the last plateau range agrees very well with that (44.95%) calculated by assuming the formation of $LaFeO_3$. In order to characterize the decomposition product in each plateau, IR and high temperature powder X-ray diffraction patterns were measured. The ν(CN) stretching bands around 2100 cm^{-1} disappear at 350 °C. Instead, the bands attributable to carbonate groups[8] are apparently observed at 1450, 1380, 1050, and 840 cm^{-1}, as shown in Fig. 2. However, from X-ray diffraction spectrum at this temperature as shown in Fig.3, the formation of a small amount of $LaFeO_3$ can be recognized.[9] The X-ray diffraction spectral intensities become more intense at 500 °C, though the IR bands due to the carbonate groups are still observed. At 620 °C, such IR bands are no longer observed and only a strong band due to the oxide appears around 550 cm^{-1}.[1d] From these observations, X-ray diffraction patterns and weight loss percentages, it is suggested that the formation of perovskite, $LaFeO_3$ is almost complete in the last plateau above 580 °C. The X-ray diffraction results indicate that the formations of Fe_2O_3 and/or La_2O_3 are not proceeded. Crystallographic data of $LaFeO_3$ obtained at 620 °C were as follows: Crystal system orthorhombic, space group Pbnm, a = 0.5554 nm, b = 0.5552 nm, c = 0.7842 nm.

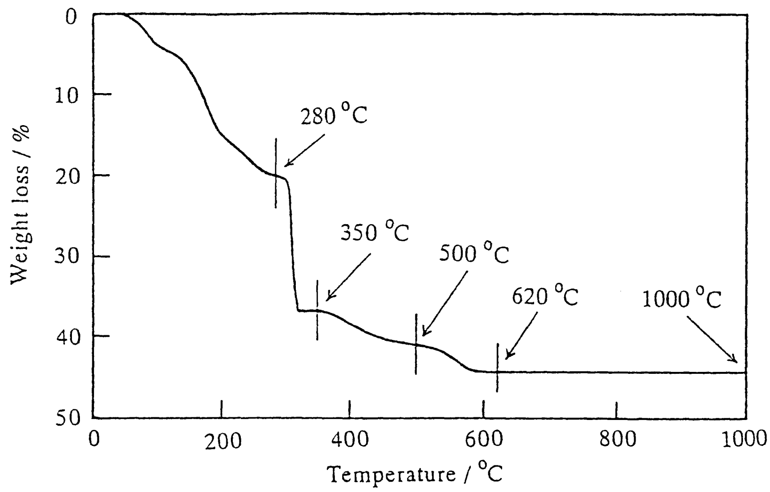

Fig.1. TG curve of $\{La[Fe(CN)_6] \cdot 5H_2O\}_x$.

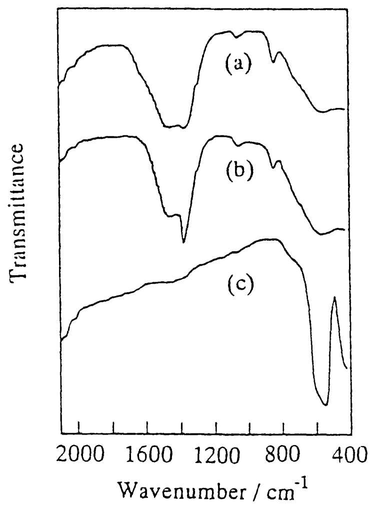

Fig.2. IR spectra of decomposition products. Decomposition temperature; (a) 350 °C, (b) 500 °C, (c) 620 °C.

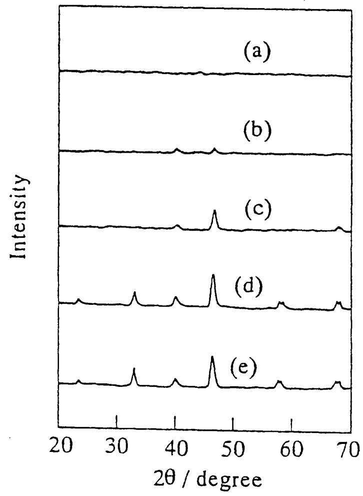

Fig.3. Powder X-ray diffraction patterns of decomposition products (CuKα). Decomposition temperature; (a) 280 °C, (b) 350 °C, (c) 500 °C, (d) 620 °C, (e) 1000 °C.

Mean particle diameter and specific surface area of $LaFeO_3$ prepared by calcining at 620 °C were estimated to be 50 nm and 22.7 m^2/g using scanning electron microscope and BET method by adsorption of nitrogen, respectively. The surface area was found to be much larger than that (2.5 m^2/g) of $LaFeO_3$ obtained by calcining the mixture of Fe_2O_3 and La_2O_3 at 1000 °C.[10] Furthermore, this value is larger than 14.4 m^2/g for the sample by citrate process and calcined at 550 °C and 4.4 m^2/g for the sample by acetate process and calcined at 850 °C reported by Yamazoe et el.[1d] As far as $LaFeO_3$ is concerned, 22.7 m^2/g is the largest among values reported so far. Thus, the present work suggests that the appropriate choice of a starting complex will be very useful for the preparation of some fine and homogeneous mixed oxides.

References

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5) The formation of complex was confirmed from powder X-ray diffraction pattern reported in "Powder Diffraction File," ed by W.F.McClune, JCPDS International Centre of Diffraction Data (U.S.A.), File No. 25-1198 and from elemental analysis. Anal. Found: C, 16.30; H, 2.19; N, 19.96%. Calcd for $C_6H_{10}N_6O_5FeLa$: C, 16.34; H, 2.29; N, 19.06%.

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9) "Powder Diffraction File," ed by W.F.McClune, JCPDS International Centre of Diffraction Data (U.S.A.), File No. 37-1493.

10) It was experimentally confirmed that the formation of perovskite-type oxide was proceeded by calcining the (1:1) mixture of Fe_2O_3 and La_2O_3 at 1000 °C, where average particle size of each oxide was 1 μm, and specific surface areas were 7 m^2/g for Fe_2O_3 and 5 m^2/g for La_2O_3.

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