Preparation of Perovskite-type $LaFe_{0.5}Co_{0.5}O_3$ by Thermal Decomposition of Heteronuclear Complex, $\{La[Fe_{0.5}Co_{0.5}(CN)_6]\cdot 4H_2O\}_x$

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Submicron perovskite-type $LaFe_{0.5}Co_{0.5}O_3$ powders were prepared by the thermal decomposition of a title cyanide-bridged heteronuclear complex. The decomposition of CN bridge begins at about 360 °C and the formation of perovskite-type oxide proceeds at a higher temperature with a gradual decomposition of carbonates. Perovskite-type $LaFe_{0.5}Co_{0.5}O_3$ with cubic structure was formed when the complex was calcined at 700 °C. By raising the calcining temperature to 900 °C, hexagonal phase was formed.

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. 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. 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] 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 some heteronuclear complexes[2-4] were used as starting complexes. Such decomposition of heteronuclear complexes is a promising method for the preparation of homogeneous perovskite-type oxides 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 $LaFe_{0.5}Co_{0.5}O_3$ obtained was characterized.

The complex, $La[Fe_{0.5}Co_{0.5}(CN)_6]\cdot 4H_2O$ ($LaFe_{0.5}Co_{0.5}$-complex), was synthesized by mixing the equivalent amounts of lanthanum(III) nitrate hydrate and a 1:1 mixture of potassium hexacyanoferrate(III) and potassium hexacyano cobaltate(III) under stirring in water. In order to characterize the complex, IR, TG and X-ray diffraction patterns (CuKα) were measured. In Fig.1, IR spectrum of $LaFe_{0.5}Co_{0.5}$-complex is shown with LaFe-complex and LaCo-complex. The ν(CN) stretching bands are observed at 2140 cm^{-1} and 2060 cm^{-1} for LaFe-complex, at 2152 cm^{-1} for LaCo-complex and at 2150 cm^{-1} with a shoulder (2140 cm^{-1}) and 2060 cm^{-1} for $LaFe_{0.5}Co_{0.5}$-complex. The ν(CN) stretching bands are observed in a higher wavenumber region than the frequencies (2120 cm^{-1} and 2045 cm^{-1}) of corresponding vibrations in $K_3[Fe(CN)_6]$. These shifts to higher frequencies indicate the coordination of nitrogen to La(III) and the construction of the three-dimensional network structure by Fe(III), Co(III)-CN-La(III) linkage.[5,6] XRD spectra of these complexes are shown in Fig.2. The observed signals of LaFe-complex and LaCo-complex are in fair agreement with JCPDS files; $La[Fe(CN)_6]\cdot 5H_2O$ (JCPDS file No.251198) and $La[Co(CN)_6]\cdot 5H_2O$ (JCPDS fileNo.360674). The figure of the XRD spectrum of the $LaFe_{0.5}Co_{0.5}$-complex is different from the results of LaFe- and LaCo-complex. These observed results suggest that the $LaFe_{0.5}Co_{0.5}$-complex is not a mixture of powders of each LaFe- and LaCo-complex.

When the sample was heated at the rate of 5 °C/min in air flow, the decomposition of $LaFe_{0.5}Co_{0.5}$-complex begins at about 50 °C, and the plateau was observed in the temperature range of 240 to 360 °C. The weight loss percentage at 280 °C was about 17.3 %, which was in good agreement with the value (17 %)

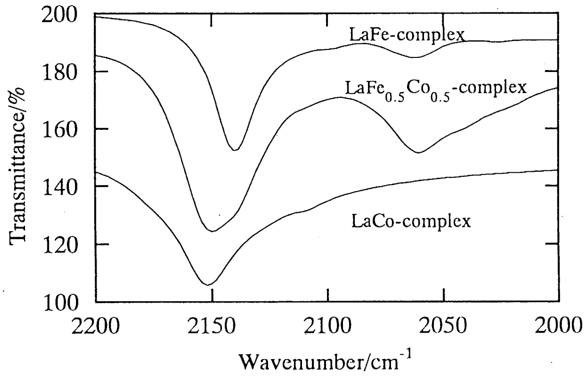

Figure 1. FT-IR spectra of $LaFe_{0.5}Co_{0.5}$-, LaFe- and LaCo-complex powders.

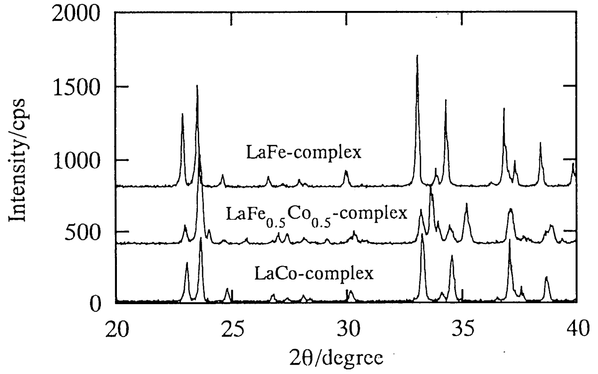

Figure 2. XRD results of $LaFe_{0.5}Co_{0.5}$-, LaFe- and LaCo-complex powders.

calculated by assuming the formation of anhydrate from La[$Fe_{0.5}Co_{0.5}(CN)_6$] • $4H_2O$. Further heating causes an abrupt weight loss due to the decomposition of cyanide group, and gradual decreases were observed up to 715 °C (TGf), followed by the last plateau. The weight loss percentage (44.29%) in the last plateau range agrees very well with that (44.95%) calculated by assuming the formation of $LaFe_{0.5}Co_{0.5}O_3$. The starting temperature of CN decomposition is in the order for LaCo-complex >$LaFe_{0.5}Co_{0.5}$-complex>LaFe-complex. The TGf of $LaFe_{0.5}Co_{0.5}$-complex is higher than that of LaCo-complex (670 °C) and LaFe-complex (650 °C) when the samples is heated at the rate of 5 °C/min in air flow. In order to characterize the decomposition product in each plateau, IR and X-ray diffraction patterns were measured. The ν(CN) stretching bands at 2150 cm^{-1} and 2060 cm^{-1} disappear at 400 °C. Instead, the bands attributable to carbonyl (1800 ~2100 cm^{-1}) and carbonate groups(1300 ~ 1700 cm^{-1}) are apparently observed as shown in Fig.3. However, from X-ray diffraction spectrum at this temperature shown in Fig.4, the formations of perovskite-type oxide as majority product, of which the lattice constants are similar to $LaFeO_3$ and of La_2CO_5, Co_2O_3 and Co_3O_4 as contaminations can be detected. The X-ray diffraction spectral intensities for perovskite-type oxide, became more intense with disappearances of the signals of La_2CO_5, Co_2O_3 and Co_3O_4 when the sample was heated at a higher temperature, though the IR bands due to the carbonate groups were observed up to 700 °C. At 800 °C, such IR bands are no longer observed and only a strong band due to the oxide appears around 600 cm^{-1}. When the complex {La[$Fe(CN)_6$] • $5H_2O$}$_x$ was decomposed at the same temperature, only $LaFeO_3$ was detected without the formations of Fe_2O_3 and/or La_2O_3. Crystallographic data of $LaFeO_3$ obtained at 800 °C were as follows: Crystal system orthorhombic, a = 0.556 nm, b = 0.785 nm, c = 0.555 nm. For the complex {La[$Co(CN)_6$] • $5H_2O$}$_X$ decomposed at the same temperature, crystallographic data of $LaCoO_3$ were as follows: Crystal system hexagonal, a = b = 0.544 nm c = 1.309 nm. For the $LaFe_{0.5}Co_{0.5}$-complex calcined at 400 °C, most of the XRD signals are detected at almost the same positions observed for perovskite-type $LaFeO_3$. With increasing the calcination temperature higher than 550 °C, some new peaks appeared at higher degrees, and developed with lowering intensity of the peaks observed for the complex calcined at 500 °C. For the complex calcined at 900 °C, the XRD spectrum is very similar to that of perovskite-type $LaCoO_3$ with hexagonal structure rather than that of perovskite-type $LaFeO_3$ with orthorhombic structure, and most of the corresponding peaks appeared at a lower degree than the corresponding peaks of perovskite-type $LaCoO_3$ as shown in Fig.4. For the complex calcined at 800 °C the XRD spectrum is different from that of the complex calcined at 900 °C and suggest the cubic structure, since the spectrum is very similar to that of $LaCo_{0.4}Fe_{0.6}O_3$ (JCPDS fileNo.400224).

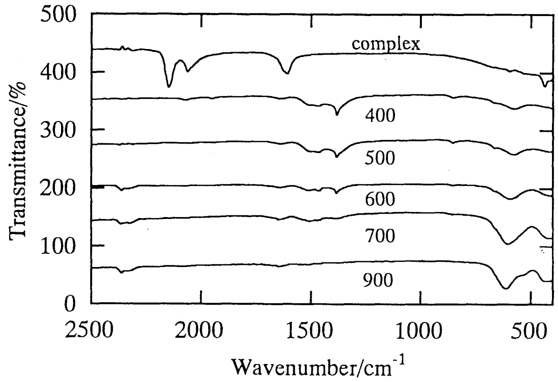

Figure 3. FT-IR spectra of $LaFe_{0.5}Co_{0.5}$-complex powders calcined at various temperatures. calcining temperature is shown in the figure.

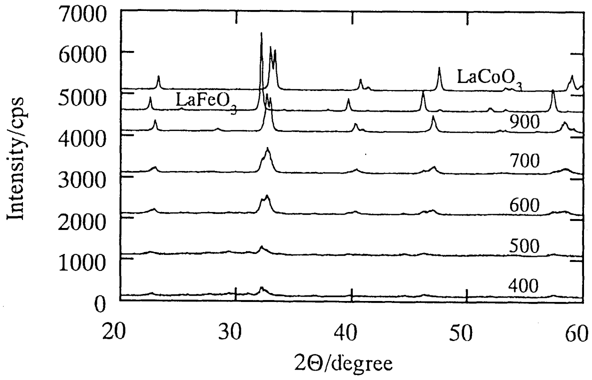

Figure 4. XRD results of $LaFe_{0.5}Co_{0.5}$-complex powders calcined at various temperatures and of $LaCoO_3$ and $LaFeO_3$. calcining temperature is shown in the figure.

Microstructure of $LaCo_{0.5}Fe_{0.5}O_3$ obtained by the decomposition of the complex at 800 °C was examined by SEM. Mean particle diameter is estimated to be 0.2 μm and sintering proceeded even at this temperature.

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References and Notes

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