Preparation of Heteronuclear $Bi_{1-x}La_x[Fe(CN)_6]\cdot n(H_2O)$ Complexes and their Thermal Decomposition

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(Received January 28, 2002; CL-020105)

The heteronuclear $Bi_{1-x}La_x[Fe(CN)_6]\cdot nH_2O$ complexes were synthesized and their crystal structures were investigated by XRD and TGA. The crystal phase was hexagonal (n = 5) for x = 1.0, and orthorhombic (n = 4) for x = 0–0.7 and their mixture (x = 0.8 and 0.9). The lattice constants for the complexes linearly increased with an increase in the x value. The single phase of the trimetallic perovskite-type $Bi_{0.5}La_{0.5}FeO_3$ was obtained by its thermal decomposition at 500 °C.

Perovskite-type oxides are promising materials for many kinds of applications. $BiFeO_3$ is one of the perovskite-type materials and the $Bi_{1-x}La_xFeO_3$ solid solution has ferroelectric properties.[1] In general, polymetallic oxides have been prepared by the conventional solid reaction method. Chemical processing such as the sol-gel method is 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. We reported that heterometallic oxides with relatively high specific surface area were formed at low temperatures when heteronuclear hexacyano-complexes were used as the precursors.[2,3] The decomposition of the heteronuclear complexes is a promising method for the preparation of homogeneous mixed oxides on an atomic level.[4] For the di-metallic BiFe-complex, $Bi[Fe(CN)_6]\cdot nH_2O$ was synthesized and its crystal structure was investigated.[5] However, the tri-metallic $Bi_{1-x}La_xFe$-complexes have not yet been reported. In addition, their thermal decomposition is expected to obtain a high quality perovskite-type material.

In this study, we synthesized the $Bi_{1-x}La_x[Fe(CN)_6]\cdot nH_2O$ complexes and the decomposed products were characterized by X-ray diffraction (XRD) and thermogravimetry analysis (TGA).

The heteronuclear complexes, $Bi_{1-x}La_x[Fe(CN)_6]\cdot nH_2O$, were synthesized at room temperature by mixing aqueous solutions of equimolar amounts of $K_3Fe(CN)_6$ and a stoichiometric mixture of $Bi(NO_3)_3\cdot 5H_2O$ and $La(NO_3)_3\cdot 6H_2O$ with continuous stirring. The resulting precipitate was collected by suction filtration and then washed with water, methanol and diethyl ether, before drying in air at room temperature.

The thermal decomposition behavior was examined by TGA analysis, performed at a heating rate of 5 °C/min in air. The heat-treated samples were prepared by holding the complex at various temperatures in ambient air for 1 h. In order to characterize 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).

Figure 1 shows the XRD results for the $Bi_{1-x}La_x$-complexes. For x = 1.0 (LaFe-complex), the XRD peak position agreed with that of $La[Fe(CN)_6]\cdot 5H_2O$, which has a hexagonal structure.[6] On the other hand, the XRD peaks showed an orthorhombic structure for x = 0–0.7.[7] This is ascribed to the difference in the water molecules of crystallization (n) in the complexes, i.e., n = 5 (x = 1.0) and n = 4 (x = 0–0.7).[8] For x = 0.8 and 0.9, a mixture of two types of complexes was confirmed by the XRD results. Figure 2 shows typical TGA results for the complexes. Dehydration of crystal by the loss of water started at about 100 °C. A weight loss due to the exothermal decomposition of the ligand (confirmed by DTA) was confirmed at around 300 °C. For x = 0 ($BiFeO_3$), the complex was completely decomposed at around 270 °C. The decomposition temperature increased with an increase in the x value. The weight loss percentages for the dehydration of water and the last plateau range were close to the theoretical values calculated by assuming the formation of perovskite-type oxides from complexes containing n = 4 for x =

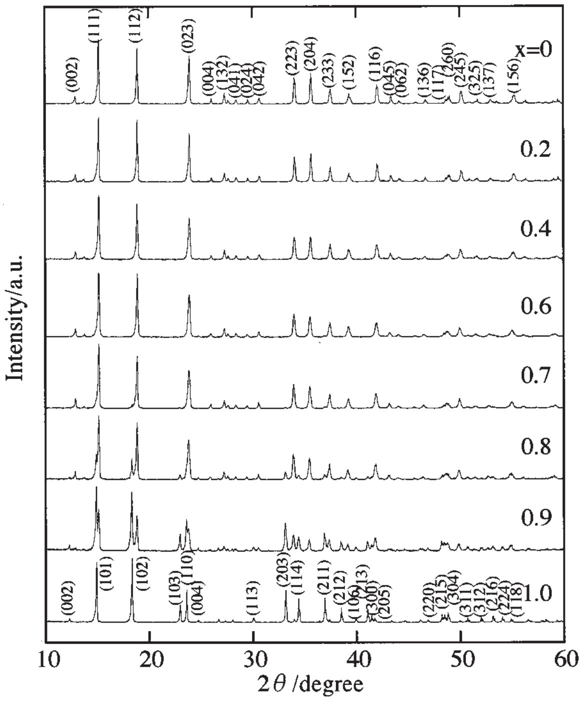

Figure 1. XRD results for $Bi_{1-x}La_x[Fe(CN)_6]\cdot nH_2O$ complexes. The x values are shown in the figure.

0 and 0.5 and n = 5 for x = 1.0 in Figure 2. Figure 3 shows the lattice constants for the complex having an orthorhombic structure. The lattice constants linearly increased with an increase in the x value for the complexes because of the larger ionic radius of the La^{3+} ion than that of the Bi^{3+} ion. However, the ionic radius of the La^{3+} ion (0.1160 nm) is smaller than that of the Bi^{3+} ion (0.117 nm) when the coordination number is eight in the complex.[9] The La^{3+} ions are surrounded by six nitrogen atoms and two H_2O molecules in the complex.[8] We presume that the ionic radius for the Bi^{3+} ion is small (0.103 nm) in the complex, because the Bi^{3+} ions are surrouned by only the six nitrogens.

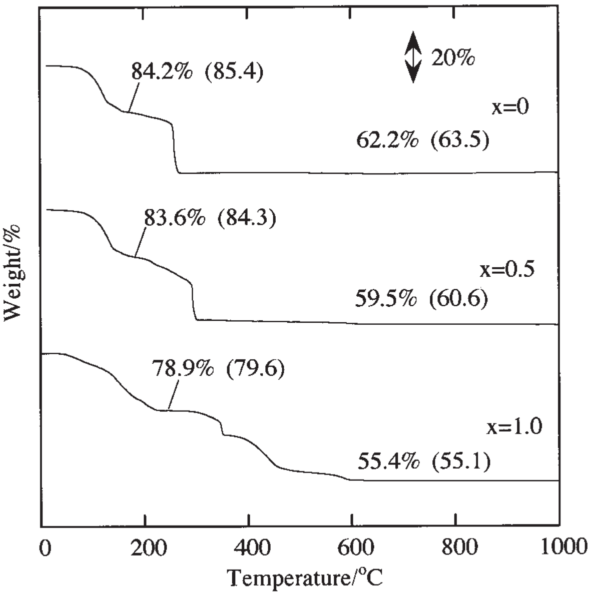

Figure 2. TGA results for $Bi_{1-x}La_x[Fe(CN)_6]\cdot nH_2O$ complexes. The weights of the experimental and (theoretical) as n = 4 (x = 0, 0.5) and n = 5 (x = 1.0) are shown in the figure.

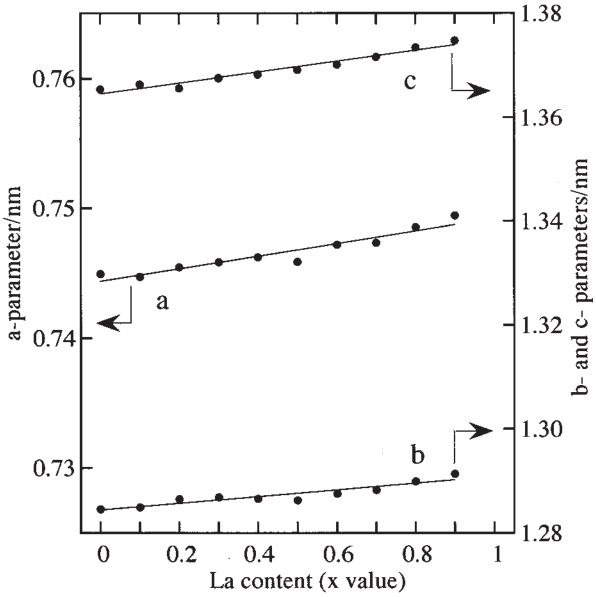

Figure 3. Lattice constants for $Bi_{1-x}La_x[Fe(CN)_6]\cdot nH_2O$ complexes (orthorhombic).

Figure 4 shows the XRD results of the thermal decomposed results for x = 0.5. The single phase of the orthorhombic trimetallic perovskite, $Bi_{0.5}La_{0.5}FeO_3$, was obtained at 500 °C.

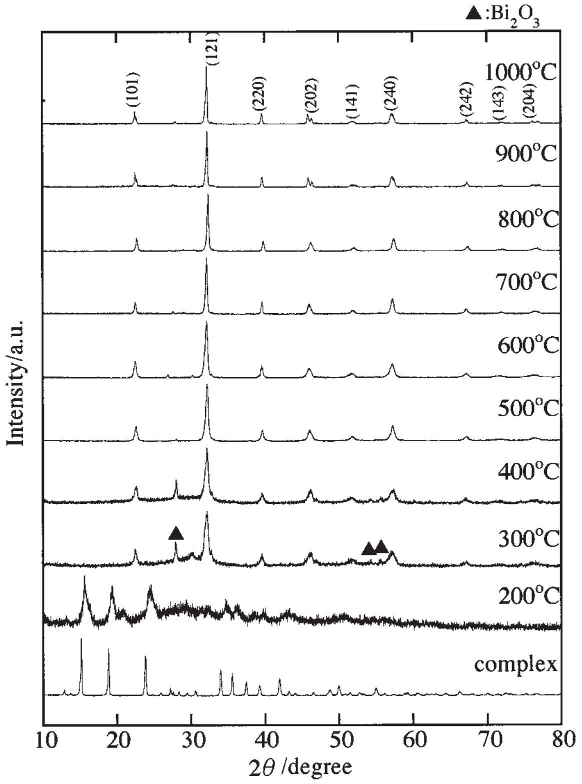

Figure 4. XRD results for the decomposed products of $Bi_{0.5}La_{0.5}[Fe(CN)_6]\cdot 4H_2O$ (x = 0.5). The decomposition temperatures are shown in the figure.

In conclusion, the heteronuclear $Bi_{1-x}La_x[Fe(CN)_6]\cdot nH_2O$ complexes were synthesized and the perovskite single phase was obtained by its thermal decomposition at low temperature. Further work will include the characterizations of the decomposed products such as homogeneity and particle size.

References and Notes

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