Hyperfine Interact
DOI 10.1007/s10751-011-0423-4

Formation and superparamagnetic behaviors of $LaFeO_3$ nanoparticles

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Abstract Formation of $LaFeO_3$ nanoparticles obtained from thermal decomposition of organometallic precursors was investigated as a function of the heat-treatment temperature. The precursors heat-treated below 300°C were amorphous, but above 350°C a single-phase of nanocrystalline $LaFeO_3$ was formed. The $LaFeO_3$ nanoparticles showed the superparamagnetic behavior in both magnetization and Mössbauer measurements. With increasing heat-treatment temperature, the crystallite size of $LaFeO_3$ nanoparticles was gradually increased. The quadrupole splitting and isomer shift of paramagnetic doublet pattern were affected by the growth of $LaFeO_3$ particles.

Keywords $LaFeO_3$ nanoparticles · Hot soap method · Superparamagnetism · Mössbauer spectroscopy

1 Introduction

Lanthanum orthoferrite, $LaFeO_3$, is one of the most common perovskite-type oxides and has been proposed for various applications such as solid oxide fuel cells, catalysts, chemical sensors, etc. [1, 2]. These properties should be enhanced by high surface area of fabricated $LaFeO_3$ particles. $LaFeO_3$ is known to be antiferromagnet with a Néel temperature T_N of 738 K [3]. However, antiferromagnetic nanoparticles often exhibit increasing net magnetization due to presence of uncompensated surface spins [4]. Recently we have reported that the $LaFeO_3$ nanoparticles exhibited considerable large magnetization at low temperature [5]. In this paper, we report the formation of $LaFeO_3$ nanoparticles obtained from thermal decomposition of organometallic

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Published online: 26 October 2011

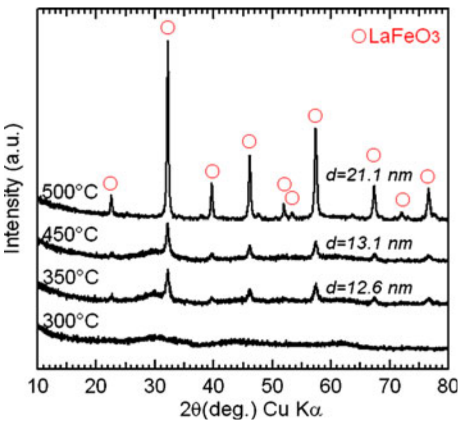

Fig. 1 XRD patterns of heat-treated samples at various temperatures. The crystallite size of $LaFeO_3$ nanoparticles evaluated from Scherrer's formula is indicated

precursors. Mössbauer spectra of $LaFeO_3$ nanoparticles were also discussed as a function of the heat-treatment temperature.

2 Experimental

Organometallic precursors for $LaFeO_3$ nanoparticles were synthesized by hot soap method. Equal amounts of iron acetylacetonate and lanthanum acetate were charged into a reaction flask with polyethylene glycol. Coordinating organic protective agents of oleic acid and oleylamine were injected into the reaction flask as well. Thereafter, the mixture was raised to 200°C and maintained for 3 h with stirring. By adding ethanol to the reaction mixture, organometallic precursors were precipitated and dried at 100°C for 1 h. For the thermal decomposition, the obtained precursors were heat-treated in air for 6 h at various temperatures between 300 and 600°C. Finally the samples were characterized by x-ray powder diffraction (XRD) with monochromatic Cu Kα, a vibrating sample magnetometer with high-sensitivity SQUID sensor and conventional transmission Mössbauer spectroscopy with a 925 MBq ^{57}Co/Rh source.

3 Results and discussion

Figure 1 shows the XRD patterns of heat-treated precursors at various temperatures. The sample heated at 300°C showed the diffuse XRD pattern with no crystalline phases. While at 350°C, broad XRD peaks attributed to the $LaFeO_3$ perovskite phase were observed. The average crystallite size estimated from the XRD peak broadening for $LaFeO_3$ particles prepared at 350°C was about 13 nm by using the Scherrer's equation. This value was fully consistent with the average grain size characterized by TEM observations. With increasing heat treatment temperature, the XRD peaks gradually became sharper and steeply intensified above 500°C because of the grain growth of the $LaFeO_3$ particles.

Room temperature Mössbauer spectra of the heat-treated samples prepared at various temperatures are shown in Fig. 2. The sample heated at 500°C, which had

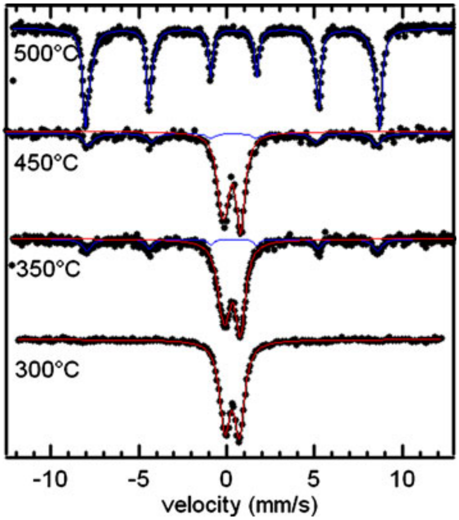

Fig. 2 Room temperature Mössbauer spectra of heat-treated samples at various temperatures. The solid lines indicate the fitted components

Table 1 Fitted Mössbauer parameters obtained from the spectra in Fig. 2

Heat temperature (°C)	Isomer shift (mm/s)	Quadupole splitting (mm/s)	Hyperfine filed (kOe)	Intensity (%)
500	0.376	–	513	100
450	0.364	–	508	23
	0.292	1.008	–	77
350	0.355	–	512	21
	0.313	0.924	–	79
300	0.327	0.824	–	100

a larger crystallite size, showed a clear sextet pattern due to antiferromagnetic ordering. However, paramagnetic doublet patterns were dominant for other samples heated at 350 and 450°C in spite of the formation of $LaFeO_3$. This behavior was attributed to superparamagnetism because of the fine crystallite size of $LaFeO_3$. The blocking temperature of about 30 K was confirmed by both magnetization and Mössbauer measurements [5]. Moreover, a large spontaneous magnetization of 7.8 emu/g was observed below the blocking temperature. The Mössbauer parameter of the doublet pattern indicated the systematic change depending on the heat-treatment temperature. The fitted parameters are listed in Table 1. The isomer shift gradually decreased while the quadrupole splitting gradually increased with increasing heat treatment temperature. This result suggested the formation of strong Fe-O bonds and ligand fields due to the crystallization of $LaFeO_3$ particles.

4 Conclusion

Nanocrystalline $LaFeO_3$ particles with an average diameter of 13 nm were prepared by thermal decomposition of organometallic precursors at 350°C. The obtained $LaFeO_3$ nanoparticles exhibited superparamagnetic behaviors. With increasing heat-treatment temperature, the grain size of $LaFeO_3$ particles was gradually increased. The values of isomer shift and quadrupole splitting were changed systematically according to the crystallization of $LaFeO_3$ particles.

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