Research Article

The Structural and Magnetic Properties of the Double Rearth Elements $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ Nanoparticles

Nguyen Thi Thuy,¹ Bach Thanh Cong,² and Dang Le Minh²

¹ Physics Department, Hue University College of Education, Hue City, Vietnam

² Faculty of Physics, Hanoi University of Science, VNU, Hanoi City, Vietnam

Correspondence should be addressed to Nguyen Thi Thuy, nguyenthithuy0206@gmail.com

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The double rearth elements $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 0.5$) nanosized powders with orthorhombic structure were prepared by sol-gel method. The particle size of the $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ powder is about 20 nm. The doping of the second rearth element in the A position of the compound ABO_3 influenced the crystalline structure and magnetic property of the samples. The $M(H)$ dependence shows that the nanosized $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ samples exhibit ferromagnetic behavior in the room temperature and the $M(H)$ curves are well fitted by Langevin functions.

1. Introduction

The vast majority of catalysts used in modern chemical industry are based on mixed metal oxides including perovskite oxides ABO_3 , where A is a rare-earth element, B is 3d transition metal that remains prominent [1]. The perovskite AFeO_3 (A = La, Y, Nd, ...) and AFeO_3 doped by transition metal elements, rare-earth elements, or alkaline earth elements show much interesting electric, magnetic phenomena. The ideal AFeO_3 is isolator and antiferromagnetic. However, the real AFeO_3 and doped AFeO_3 are electrical conduction like semiconductor and ferromagnetic, and these materials have important applications in modern telecommunication and fabricating electrical accessories. Especially, nanosized AFeO_3 and doped AFeO_3 compounds can be used in fabricating ethanol sensors, methane sensors in mining galleries, and so forth. The orthoferrite LaFeO_3 has been researched in many laboratories in the world as a catalyst in synthesizing fuel gas using in aerospace industry, pure fuel and nanosized powder LaFeO_3 can be used as a strong catalyst in synthesizing H_2 or in removing acid salicylic and axit sulfonic salicylic in sewage water, or in producing electrodes at high temperature (SOFC), and so forth [2–9].

The perovskite materials LaFeO_3 used in synthesizing gas sensors can be prepared by different chemical methods: coprecipitation method, sol-gel method, hydrothermal, sonochemical synthesis [10], and so forth. The sol-gel method is used broadly due to its advantage in which precursors can be admixed at atomic scale. The products prepared by sol-gel method are pure, homogeneous, small grain size, great surface area, and compatible with synthesizing gas sensors [11].

In this paper, $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 0.5$) in which the A position was occupied by double rearth elements was prepared by citrate-gel method. In addition to investigating the crystalline structure of the material, we also investigated the influence of the grain size on the magnetic property.

2. Experimental

In the sol-gel method, the analytical grade $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and citric acid (CA) $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ were used as starting materials. The same mole equivalent amounts of metal nitrates were weighed according to the nominal composition $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 0.5$) and then dissolved in distilled water. The citric

FIGURE 1: XRD patterns of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ nanoparticles after being annealed at 500°C for 10 hours.

acid with the ratios $(\text{CA})/\Sigma(\text{Metal ions}) = (1.2-1.5)$ was then proportionally added to the metal nitrates solution. In the above ratio, (CA) and Σ (metal ions) are concentration of (CA) and sum of concentration of metallic ions, respectively. The solution was concentrated by evaporation at $60-700^\circ\text{C}$ with continuous stirring and pH controlled by NH_3 solution. After six hours, we obtained organic gel in dark green. This gel mixture was dried at 150°C in 10 hours to obtain xerogel. The organic substances and nitrate were heated at 300°C for 4 hours to be decomposed. The nanocrystals of perovskite $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 0.5$) were obtained by decomposition of the dried gel complex at 500°C for 10 hours in air.

The determination of structural characterization was performed by means of X-ray diffraction using D5005 diffractometer with $\text{Cu K}\alpha$ radiation and 2θ varied in the range of $10-70^\circ$ at a step size of 0.02° . The particle size and morphology of the calcined powders were examined by SEM (S-4800) (Hitachi, Japan). The magnetic parameters were determined by VSM-LakeShore 7404 (LakeShore, USA).

3. Result and Discussion

X-ray diffraction patterns of the samples $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($x = 0$ to $x = 0.5$) are shown in Figure 1. Based on the diffraction peaks, we can see that all samples are the single phase with standard orthorhombic structure of LaFeO_3 and belong to the Pnma space group. Figure 2 shows the dependence of the lattice parameter a on the Nd-doping content, and the value of a was decreased with increasing in Nd content. In addition, the diffraction peaks at angle $2\theta = 32^\circ$ tend to shift toward the larger angle. This shift demonstrates that the lattice parameters decrease with increasing of Nd-doping content. The top right side of Figure 2 shows the diffraction peaks at angle $2\theta = 32^\circ$ of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ samples ($x = 0.0; 0.1; 0.15; 0.20; 0.30; 0.50$). The lattice distortion may be caused by the difference of radius of Nd^{3+} ($0.127 \text{ \AA}$) and La^{3+}

FIGURE 2: a -cell parameter versus Nd content. The part in the right hand side of the peak at around $2\theta = 32^\circ$ shows that the peak is shifted to higher reflected angel with increasing Nd concentration.

($0.136 \text{ \AA}$). It leads to the decreasing of the lattice parameters with increasing of the Nd concentration.

Table 1 shows the crystalline sizes D (nm) of the samples calculated by Scherrer formula:

$$D = \frac{k\lambda}{B \cos \theta}, \quad (1)$$

where D is the average size of crystalline particle, assuming that particles are spherical, $k = 0.94$, λ is the wavelength of X-ray radiation, B is full width at half maximum of the diffracted peak, and θ is angle of diffraction.

Figure 3 shows the SEM images of the samples with $x = 0.1; 0.2; 0.3; 0.5$ calcined at 500°C for 10 h in air. It can be estimated from Figure 3 that the average particle size is about 20 nm. Figure 4 shows that the $(M-H)$ curves of the prepared nanosized $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ were measured in the maximum magnetic field up to 1.5 T at 300 K. We can see that the samples were not magnetized to the saturated state. The $(M-H)$ curves of samples $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ ($0 \leq x \leq 0.5$) showed that the samples are ferromagnetic at room temperature.

Magnetic properties of nanosized samples are much influenced by grain size. With increasing grain size D , the coercivity H_c was increased following the law of ($H_c \sim D^6$) [12, 13]. The ferromagnetic materials are in nano-size of about single domain, and they have the superparamagnetic state with $H_c = 0$, $M_r = 0$, and $S = (M_r/M_s) = 0$ [14]. Nevertheless, the ferromagnetic materials are of multidomains size, and the value of H_c , M_r , and S will be different from zero. Clearly, based on the value of H_c , M_r , and S , we can discuss the limited size of single domain, the homogeneity of the nanosized particles and magnetic property existing in the ferromagnetic nanosized samples. From Table 2, we can see that the magnetic property of the $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ samples is similar with superparamagnetic state and the values of

FIGURE 3: SEM micrograph of (a) LaFeO_3 ; (b) $\text{La}_{0.8}\text{Nd}_{0.2}\text{FeO}_3$; (c) $\text{La}_{0.7}\text{Nd}_{0.3}\text{FeO}_3$; (d) $\text{La}_{0.5}\text{Nd}_{0.5}\text{FeO}_3$.TABLE 1: The crystalline sizes D (nm) of the samples calculated by the Scherrer formula.

Samples	$x = 0.00$	$x = 0.10$	$x = 0.15$	$x = 0.2$	$x = 0.3$	$x = 0.5$
D (nm)	20.3	16.9	19.6	16.4	21.3	19.3

TABLE 2: Characteristic values of hysteresis loops $M(H)$.

X	$M_r \cdot 10^{-3}$ (emu/g)	(M_r/M_s)	H_c (T)
$x = 0.0$	0.101	0.046	0.005
$x = 0.1$	0.103	0.053	0.001
$x = 0.15$	0.509	0.010	0.012
$x = 0.2$	0.214	0.074	0.001
$x = 0.3$	0.227	0.075	0.010
$x = 0.5$	0.235	0.080	0.011

both the remanent magnetizations (M_r) and $S(M_r/M_s)$ are approaching zero.

In order to explain the magnetic property of the samples, it can be assumed that it can be contributed partly by superparamagnetic grains. It is suggested that samples were annealed for a long time that caused the inhomogeneity in the grain sizes and the total magnetization of the samples is considered as the sum of two components:

$$M(H) = M^{\text{sp}}(H) + M^f(H), \quad (2)$$

where $M^{\text{sp}}(H)$ is the contribution from the superparamagnetic (sp) nanoparticles (single domains), and $M^f(H)$ is the

contribution of ferromagnetic (f) nanoparticles (multiple domains).

$$M^f(H) = \frac{2M_s^f}{\pi} \tan^{-1} \left[\frac{H \pm H_c}{H_c} \tan \left(\frac{\pi S}{2} \right) \right], \quad (3)$$

where M_s^f is saturation magnetization of ferromagnetic phase ($M_s^f = M_r/0.866$), and S is rectangular coefficient of ferromagnetic hysteresis loop.

The noninteraction magnetization process of the superparamagnetic monodisperse nanoparticles is commonly defined by the expression

$$M(H) = M(\infty) L \left[\frac{mH}{k_B T} \right], \quad (4)$$

where m is particle magnetic moment and $L(x) = \coth(x) - 1/x$ is the Langevin function, $x = mH/k_B T$ [14, 15]. To take into account the size dispersion effects that are always presented in any real system, the magnetization of superparamagnetic particles, in this case, is better described by following expression:

$$M^{\text{sp}}(H) = M^{\text{sp}}(\infty) \sum_j f(m_j) L \left[\frac{m_j H}{k_B T} \right], \quad (5)$$

where m_j is magnetic moment of the particle, and $f(m_j)$ is weighted terms of the Langevin functions [16].

FIGURE 4: The $M(H)$ curves of the nanosized $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ samples.

FIGURE 5: The result of the fitting of the $M(H)$ curves of prepared nanosized $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ based on the Langevin function.

It is suggested that the particles have spherical shape, then the distribution function of particle size $f(D)$ is given by expression [17]

$$f(D) = \frac{1}{\sqrt{2\pi}\sigma D} \exp\left(-\frac{\ln(D/\bar{D})^2}{2\sigma^2}\right), \quad (6)$$

where σ is standard deviation and $\bar{D}$ is the average particle size.

Because the magnetic moment of a nanoparticle depends on its shape and size, it is proposed that $f(m_j)$ has the same form like $f(D)$. Then, $f(m_j)$ can be derived from (6) knowing the average particle size $\bar{D}$. Figure 5 shows the Langevin function fitting result for the magnetization curves of the nanosized $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$.

4. Conclusion

We have investigated the effect of Nd dopant on the structural and magnetic properties of $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$. The compounds with orthorhombic single phase can be formed until $x = 0.5$. With the Nd doping, the crystalline particle size decreases and the lattice structure is strongly distorted. It leads to the variation of the magnetic property of the samples. The nanosized $\text{La}_{1-x}\text{Nd}_x\text{FeO}_3$ system has superparamagnetic behavior and can be fitted by the Langevin functions with size-dependent distribution function.

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