Hue University Journal of Science: Natural Science
Vol. 129, No. 1B, 25–29, 2020

pISSN 1859-1388
eISSN 2615-9678

MAGNETIC PROPERTY OF NANOPARTICLE $La_{1-x}A_xFeO_3$ (A = Y, Nd) PREPARED BY HIGH - ENERGY MILLING METHOD

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(*Received: 26 December 2019; Accepted: 16 March 2020*)

Abstract. Perovskite ABO_3 is a kind of the material possessing various interesting electric and magnetic properties, and these properties can be changed dramatically by doping with rare-earth metals. In this paper, nanocrystalline $La_{1-x}Y_xFeO_3$ and $La_{1-x}Nd_xFeO_3$ ($0 \leq x \leq 0.3$) were prepared by using the high-energy milling method. The X-ray diffraction (XRD) analysis reveals that the doped samples are single-phased with orthorhombic structure. The average size of particles, calculated according to the Scherrer equation, is about 16 nm. The doping of Y and Nd into the A position of ABO_3 affects the structure and magnetic properties of the material. The magnetic properties of $La_{1-x}A_xFeO_3$ exhibit clearly in the hysteresis loop M(H), measured at room temperature. The samples show weak ferromagnetic properties, close to the superparamagnetic state at room temperature.

Keywords: perovskite materials, magnetic property, nanoparticle $La_{1-x}A_xFeO_3$, high-energy milling method, XRD

1 Introduction

At high temperatures, perovskite-type $LaFeO_3$ exhibits weak ferromagnetic properties due to the change in conductivity in doped $LaFeO_3$ materials. This material has important applications in the field of modern telecommunications and electronic devices. At nanometer size, $LaFeO_3$ and its doped compounds are used mainly in the manufacture of sensors for measuring the concentration of alcohol and methane in mines. Especially, recently in the world, as well as in Vietnam, many scientists have been applying nanotechnology and nanoscience in nano research and applications in the pharmaceutical industry that may including advanced drug delivery systems, new therapies, and in vivo imaging. The properties of the obtained sample depend greatly on the manufacturing method, and therefore it is necessary to improve the sample fabrication. Using the high-energy milling method, we synthesized $LaFeO_3$ crystal powder with an average size of about 16 nm at 500 °C [1-5].

In this paper, the nano perovskite $La_{1-x}A_xFeO_3$ sample systems (A = Y, Nd), with x = 0, 0.1, 0.3, were successfully fabricated. The doping of rare earth elements Y or Nd causes the perovskite structure to be distorted, leading to the appearance of a covalent mixed state that strongly affects the of the manufactured materials. The sample system shows the magnetic properties close to the superparamagnetic state at room temperature.

2 Experimental

The sample system $La_{1-x}A_xFeO_3$, with A being Y, Nd, and x = 0, 0.1, 0.3, was manufactured by using the high-energy milling method. All the chemicals used in the present study are of analytical grade

(96–98% purity) and purchased from National China Chemical Corporation. A mixture of La_2O_3, Y_2O_3, and Nd_2O_3 was prepared with the nominal composition, and the oxides are mixed in distilled water for 8 hours. The powders were dried, pressed into cylindrical tablets, and incubated at 200 °C. Then, the samples were pulverized into nanopowders with SPEX 8000D high-energy grinding device for 5 hours. The powders were further pressed into cylindrical tablets of 1 cm in diameter under high pressure. The sample is finally heated at 500 °C for 10 hours.

The structure of the materials was studied via the X-ray diffraction with the D5005-Bruker-Germany diffraction device. The hysteresis curves M(H) were measured on the vibration magnetometer VSM LakeShore 7404 (LakeShore, USA) in magnetic field of 1.3 T at room temperature.

3 Result and discussion

The X-ray diffraction patterns of $La_{1-x}Nd_xFeO_3$ and $La_{1-x}Y_xFeO_3$ are shown in Fig. 1 for $x = 0$ to $x = 0.3$. All reflections can be indexed within the orthorhombic symmetry, space group *Pnma*. The absence of impurity lines proves high phase purity and the success of the high-energy milling method in stabilizing the *Pnma* structure for the Y content between 0 and 0.3 [6-8]. From Fig. 1, we see that the width of the diffraction peaks is relatively big, indicating that the size of particles is small.

As can be seen in Fig. 1, sharp diffraction peaks indicate that the fabricated samples are single-phased. Particularly, for the sample $La_{0.7}Y_{0.3}FeO_3$, it is not possible to observe clear peaks. This means that the doped sample Y with the doping concentration $x = 0.3$ did not form the perovskite phase.

X-ray diffraction data show that these samples have orthogonal patterns (orthorhombic). The average particle size of about 16 nm is calculated from the Scherrer formula (1)

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

where D is the average particle size; $k = 0.94$ is the Scherrer constant; $\lambda = 0.158406$ nm is the X-ray wavelength; B is the width of the maximum peak at half the height of the peak; θ is the diffraction angle.

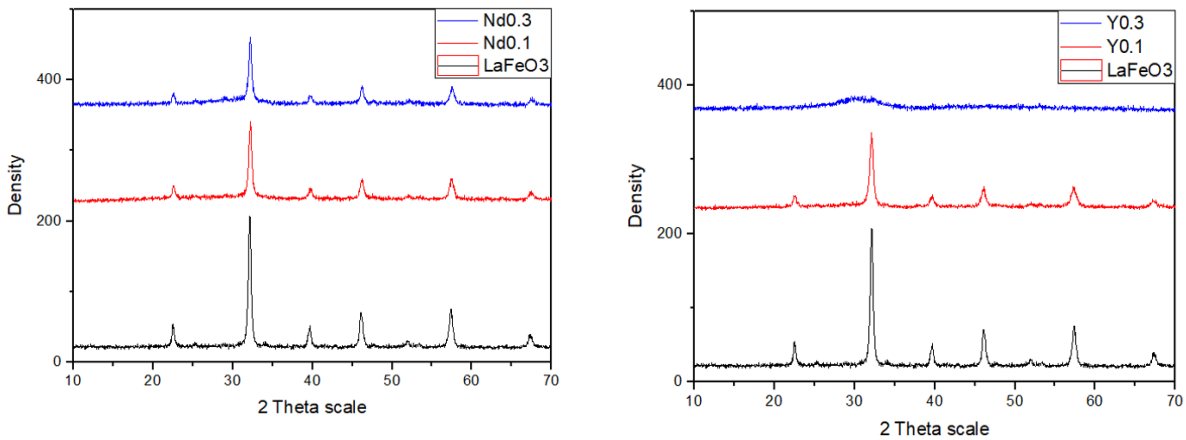

Fig. 1. X-ray diffraction diagram of the material systems $La_{1-x}Nd_xFeO_3$ and $La_{1-x}Y_xFeO_3$ (with $x = 0$, $x = 0.1$ and $x = 0.3$)

pISSN 1859-1388
eISSN 2615-9678

The relatively small size of $La_{0.1}Y_{0.9}FeO_3$ (13 nm) and $La_{0.9}Nd_{0.1}FeO_3$ (15 nm) (Table 1 and Table 2), samples open numerous applications in the future, especially in biomedicine for cell extraction and drug transmission in a simple, cheap method at low temperatures.

Fig. 2 presents the hysteresis curves of nanomaterial $La_{1-x}A_xFeO_3$ (A = Y, Nd) (x = 0; 0.1; 0.3) at room temperature with the external magnetic field of 1.3 T. Normally, $LaFeO_3$ is known to be antiferromagnetic, having a G-type magnetic structure. However, the magnetization-magnetic field (M(H)) curves of the prepared nano $La_{1-x}A_xFeO_3$ measured in the maximum magnetic field of 1.3 T show that the materials have weak ferromagnetism. This could be due to the canted spins structure (canted antiferromagnetic) and moreover, the oxygen deficiency can occur during heating the sample at high temperatures [1].

Table 1. The average particle size of the material systems $La_{1-x}Y_xFeO_3$

x	Formula	B (rad)	θ (degree)	D (nm)
0	$LaFeO_3$	0.0086	22.653	18
0.1	$La_{0.9}Y_{0.1}FeO_3$	0.0095	11.297	13
0.3	$La_{0.7}Y_{0.3}FeO_3$	–	–	–

Table 2. The average particle size of the material systems $La_{1-x}Nd_xFeO_3$

x	Formula	B (rad)	θ (degree)	D (nm)
0	$LaFeO_3$	0.0086	22.653	18
0.1	$La_{0.9}Nd_{0.1}FeO_3$	0.0101	22.127	15
0.3	$La_{0.7}Nd_{0.3}FeO_3$	0.0091	22.151	17

For the $La_{1-x}Y_xFeO_3$ (x = 0.1) and $La_{1-x}Nd_xFeO_3$ (x = 0.3) samples, the curve of M(H) is more vertical than that of the others, indicating the samples are easier to magnetize. This could be the result of the crystal anisotropic effects.

When the magnetic field returns to 0, the magnetic moment remains non-zero. The area of the S shape in the graph is the work done by the magnetic force. The bigger the distance between the intersection of the curves and the horizontal axis, the higher the dissipated energy of magnetic material will be. The fact that the properties changing from antiferromagnetism to weak ferromagnetism or normal ferromagnetism can be explained by the following reason: the process of burning materials at high temperatures for a long time leads to the lack of oxygen in the molecular structure, forming a mixed valency Fe^{3+}/Fe^{2+} and Y^{3+}/Y^{2+} or Fe^{3+}/Fe^{2+} and Nd^{3+}/Nd^{2+} with different magnetic moments.

The value of M_s increases proportionally to the ratio of Y or Nd-doped (Tab. 3). The maximum value of M_r/M_s ratio for $La_{1-x}Y_xFeO_3$ system is 0.035 at x = 0.1, and for $La_{1-x}Nd_xFeO_3$ system is 0.074363 at x = 0.3. The ratio of M_r/M_s of Y-doped samples is smaller.

The M_r/M_s ratio near zero indicates that these materials have weak ferromagnetism and close to superparamagnetic states. The compounds La_2O_3, Y_2O_3, and Nd_2O_3 are anti-magnetic materials; therefore, the none-zero values of M_r/M_s could be the result of mixed Fe^{3+}/Fe^{2+} and Y^{3+}/Y^{2+} or Fe^{3+}/Fe^{2+} and Nd^{3+}/Nd^{2+} with different magnetic moments [2, 7, 9]. As a consequence, the materials have weak ferromagnetism. Furthermore, the crystalline deformation of the materials that form antiferromagnetism does not contribute to the weak ferromagnetic properties of the material.

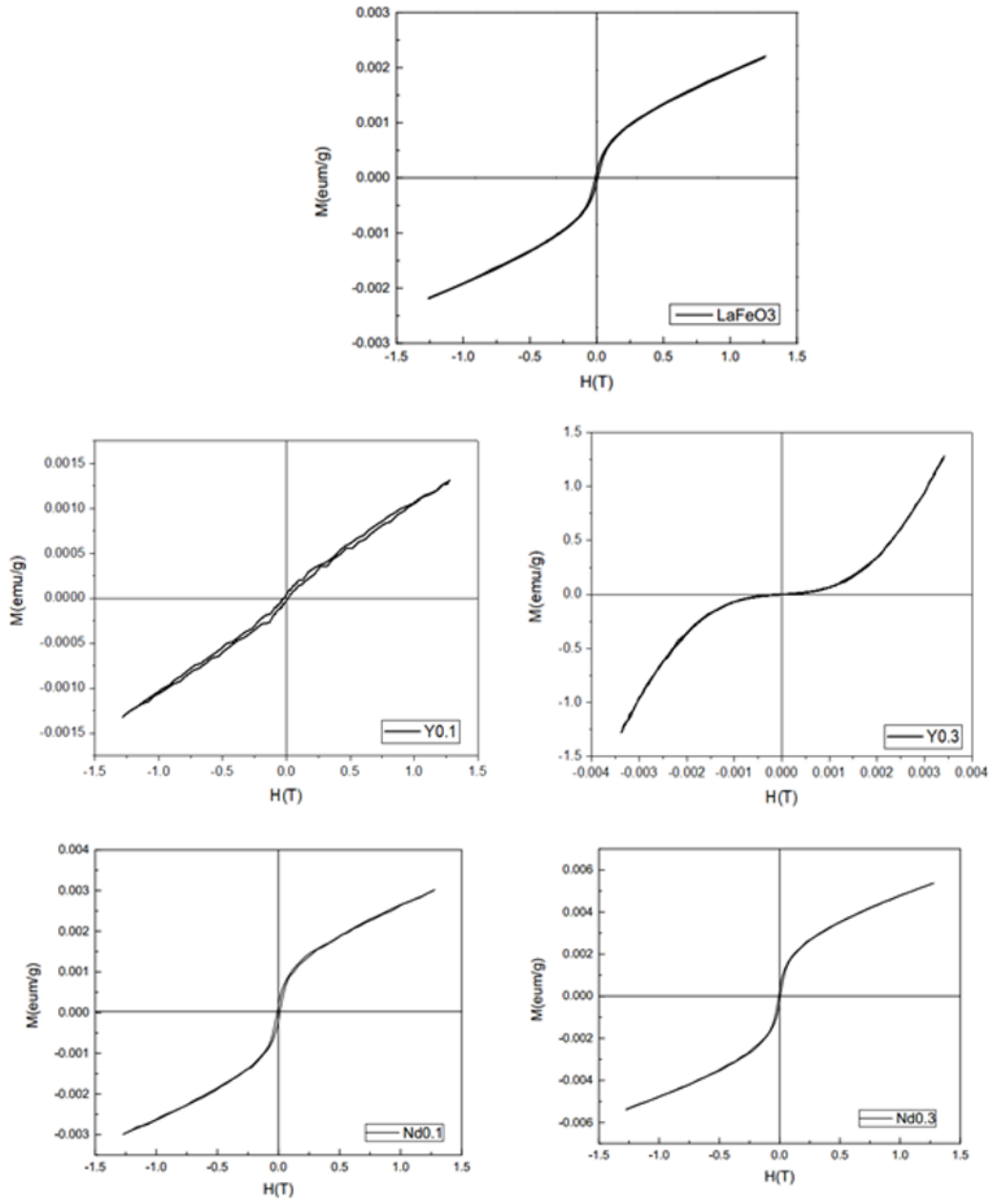

Fig. 2. Hysteresis curve *M*(H) of Y or Nd-doped the material systems $LaFeO_3$

Table 3. Characteristic values of hysteresis loops *M*(H) of the material systems $La_{1-x}Y_xFeO_3$ and $La_{1-x}Nd_xFeO_3$

x	Formula	M_s	M_r	M_r/M_s
0	$LaFeO_3$	0.000100	0.002210	0.046
0.1	$La_{0.9}Y_{0.1}FeO_3$	0.000046	0.001310	0.035
0.3	$La_{0.7}Y_{0.3}FeO_3$	0.000210	0.003410	0.062
0.1	$La_{0.9}Nd_{0.1}FeO_3$	0.003023	0.000227	0.075091
0.3	$La_{0.7}Nd_{0.3}FeO_3$	0.005379	0.0004	0.074363

pISSN 1859-1388
eISSN 2615-9678

4 Conclusion

Nanocrystals of perovskite-type $La_{1-x}Y_xFeO_3$ and $La_{1-x}Nd_xFeO_3$ were successfully manufactured by using the high-energy milling method with an average particle size of 16 nm. The magnetic properties of $La_{1-x}Y_xFeO_3$ and $La_{1-x}Nd_xFeO_3$ samples exhibit clearly in the hysteresis loop *M*(H) measured at room temperature. The samples show weak ferromagnetic properties close to the superparamagnetic state at room temperature. This result could be a potential of applications in the field of drug transmission through superparamagnetic nanoparticles.

Funding statement

This work was supported by University of Education, Hue University Foundation for Science and Technology Development code: T.19-TN-09

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