EXTRAORDINARY MAGNETIC PROPERTIES OF $LaFeO_3$ SYSTEM DOPED Ti, Co, Cu

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Abstract: $LaFeO_3$ system with doped Ti, Co, Cu was manufactured by solid state reaction method, it was sintered at 1250^0C and 1290^0C in 10 hours with a heating rate of 3^0C/min. Using X-ray diffraction and Scanning Electron Microscope (SEM) to examine the structure, it reveals that samples are single-phase and orthogonal-perovskite structure describing by the Pnma space group, the unit cell volume of the samples increases when Ti, Co, Cu are doped to replace ion Fe^{+3}. The size of particle increase while raising the temperature of sintering. Doping Ti, Co, Cu ions has strongly changed the magnetic properties of the sample system. Magnetic hysteresis loops M(H) and magnetocaloric M(T) of the samples are measured in different magnetic fields and show interesting results. All the samples shown strong ferromagnetism, among which $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ shown the strongest and its Curie temperature is about 450^0C.

Keywords: $LaFeO_3$ doped Ti, Co, Cu; magnetic hysteresis loop M(H); magnetocaloric loop M(T); strong ferromagnetism

1. INTRODUCTION

Perovskite material has the general form ABO3 with A is the cation of rare earth element or alkaline earth metals (Y, La, Nd, Sm, Ca, Ba....), B is the cation of transition metal (Mn, Co, Fe). The replacement of different elements into position of A or B or simultaneously replacing two positions can create lots of change in nature. When there is a doping, the electric property of perovskite materials has a lot of promising improvements to suit different application purposes. Studies on the manufacture and investigating perovskite materials have been made with familiar families of materials such as $SrTiO_3$, $LaMnO_3$, $CaMnO_3$, $LaFeO_3$… [1-8]. When part of the ion of Ln (rare earth element), Mn or Co is replaced by ions of lower or higher valence, there exist a valence mixture state (Mn^{3+}/Mn^{4+}, Co^{3+}/Co^{4+} or Fe^{3+}/Fe^{4+}). The structure is distorted, which leads to the appearance of some special magnetic properties or some important magnetic effects namely, Giant Magneto Resistance – GMR, Collosal Magneto Caloric Effect – CMCE. These promise to bring many applications in electronics, information, radio telecommunication, magnetic cooling which does not pollute the environment.

2. MATERIALS AND METHODS

The sample LaFeO3 doped Ti, Co, Cu is manufactured by solid state reaction method, oxides La_2O_3(99.5%), Fe_2O_3(99%), Co_2O_3(99%), TiO_2(99%), CuO(99%) are blended

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followed the nominal component, mixture was crushed and mixed once in 12 hours with distilled water then compressed into cylindrical pellets ($\Phi = 10mm, h = 10mm$) and conducted preliminary calcination at 900°C in air for 8 hours. During the calcinating process, the reaction between the ingredients in batches, occur at high temperatures to form solid solution. After preliminary calcination, samples were crushed in dry and wet way for 5 hours. After the material was crushed the second time, it was well mixed with 2% of binder which is PVA solution. Next the sample was pressed into the block which has size $12mm \times 4mm \times 3mm$ and put into sintered at 1290 °C for 10 hours with a heating rate of 3°C/min. The sample, then, is cooled under the oven.

The structure was investigated by using X-ray diffraction via diffractometer D5005 which uses K_α radiation of the copper element and the diffraction angle 2θ varied from 10 to 70° with each step of 0.02°. The M(H) and M(T) loop are measured in the magnetic field from 2 Tesla in room temperature up to 900°C on the MicroSense Easy VSM Software version 20130321-02 of the Institute of Advanced Science and Technology (AIST), Polytechnic University of Hanoi.

3. RESULTS AND DISCUSSIONS

X-ray diffraction patterns of $LaFeO_3$ system doping Ti, Co, Cu are presented in Figure 1 and Figure 2. The clear sharp peaks are assigned to be single-phase of the orthogonal-perovskite structure describing by the Pnma space group.

According to the results of X-ray diffraction, lattice parameters and unit cell volume of the samples are calculated and presented in Table 1 and Table 2. It can be seen from the data that the unit cell volume of samples increases while replacing ion Fe^{+3} by ion Ti^{+4}, Co^{+3}, Cu^{+2}. The reason is that the radius of ion Ti^{+4} (r = 0,650 Å), Co^{+3} (r = 0,648 Å) and Cu^{+2} (0,730 Å) is larger than the radius of ion Fe^{+3} (r = 0,645 Å). The crystal lattice deformation when doping Ti^{+4}, Co^{+3}, Cu^{+2} into $LaFeO_3$ is the main reason affecting the magnetic properties of samples.

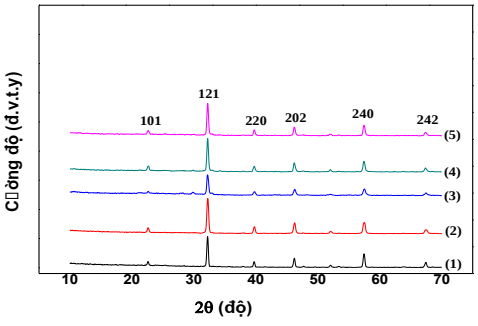


Fig. 1. *X-ray diffraction diagram of sample* sintered at *1290⁰C: $LaFeO_3$ (1), $La(Fe_{0,6}Ti_{0,4})O$, $La(Fe_{0,5}Ti_{0,5})O_3$ (3), $La(Fe_{0,4}Co_{0,1}Ti_{0,5})O_3$ (4) $La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$ (5)*

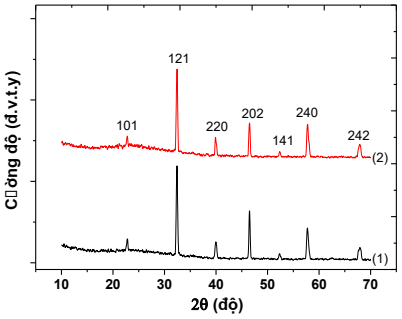


Fig. 2. *X-ray diffraction diagram of $La(Fe_{0,4}Cu_{0,1}Ti_{0,5})O_3$ sintered at 1230⁰C (1) and 1250⁰C(2)*

Table 1. *Lattice parameters, unit cell volume of sintered samples at 1290^{0}C*

Compound	a(**Å**)	b(**Å**)	c(**Å**)	α	β	γ	V(**Error! Reference source not found.**)^3
$LaFeO_3$	5,570	5,532	7,890	90^o	90^o	90^o	243,1
$La(Fe_{0,6}Ti_{0,4})O_3$	5,596	5,531	7,892	90^o	90^o	90^o	244,3
$La(Fe_{0,5}Ti_{0,5})O_3$	5,664	5,532	7,892	90^o	90^o	90^o	247,3
$La(Fe_{0,4}Co_{0,1}Ti_{0,5})O_3$	5,672	5,532	7,896	90^o	90^o	90^o	247,8
$La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$	5,683	5,534	7,910	90^o	90^o	90^o	248,8

Table 2. *Lattice parameters, unit cell volume of $La(Fe_{0,4}Cu_{0,1}Ti_{0,5})O_3$, sintered at 1230^{0}C and 1250^{0}C*

Temperature	a(**Error! Reference source not found.**)	b(**Error! Reference source not found.**)	c(**Error! Reference source not found.**)	α	β	γ	V(**Error! Reference source not found.**)^3
1230^{0}C	5,586	5,531	7,885	90^o	90^o	90^o	243,6
1250^{0}C	5,596	5,532	7,890	90^o	90^o	90^o	244,3

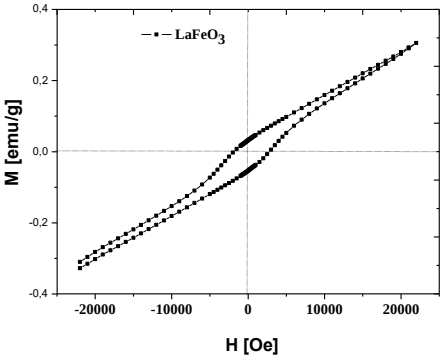
Figure 3 is SEM images of Ti and Co doped samples, sintered at 12900C. The size of the particles is quite homogeneous. Figure 4 is SEM images of Ti and Cu doped samples, sintered at 1230^{0}C and 1250^{0}C. In the sample with CuO, whose fusion temperature is low, the diffusion process is enhanced by solid state reactions with the presence of liquid phase. The process of reaction is better and the particle size is larger, which leads to the increase of sample density. In Figure 4, the shape of particles is nearly single crystal.

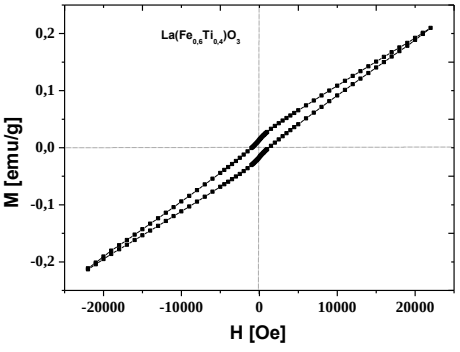
According to Fig.5 and Table 3, all the samples behave as ferromagnetism. Among which, $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ shows stronger ferromagnetism than two others samples. Its magnetic hysteresis loop is more vertical, which means it can be magnetized more easily [9-14]. Theoretically, magnetization of the sample will decrease when doping Cu into $La(Fe_{0.5}Ti_{0.5})O_3$ since ion Cu^{+1} and Cu^{+2} both show paramagnetism. However, magnetization of the sample increases drastically when doping Cu. This extraordinary phenomenon can be explained by the rapid increase of the sampling density when CuO is contained in the sample.

Figure 6 and figure 7 is the M(T) loop of $La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$ measured at magnetic field 100 Oe and 1T respectively. The M(T) loop in Figure 6 is considered to be interesting as the magnetization is negative (M<0) in the temperature range from room temperature to about 200^0C and increases as the temperature rises. We assume that since the magnetizing magnetic field is too small, the magnetizing energy is not big enough to create ferromagnetic order. It can only create an inducing magnetization, which is opposite to external magnetic field and negative same as the magnetization of diamagnetic material. When increasing the temperature, thermoenergy and magnetic energy will increase big enough to create ferromagnetic order. In this case, at the temperature higher than 200^0C, the sample behaves as ferromagnetism and the magnetization is proportional to temperature by the Hopkinson effect (the M(T) loop at the temperature range higher than 200^0C (Fig. 6)), from which the Curie temperature is established at about 500^0C. In figure 7, magnetizing magnetic field 1Tesla is high enough to create ferromagnetic order at room temperature, thus the magnetization of sample at room temperature is positive and the Curie temperature is about 500^0C [15-18].

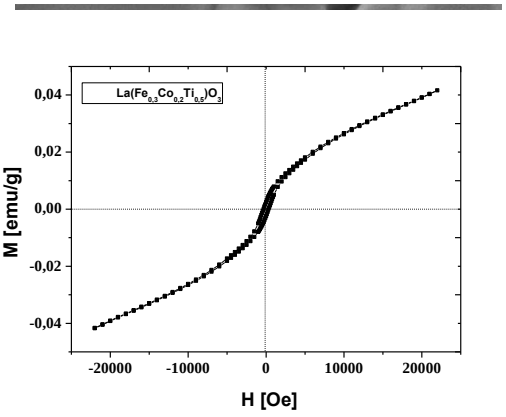
Table 3. *Magnetic hysteresis loop parameters of $LaFeO_3$(a), $La(Fe_{0,6}Ti_{0,4})O_3$(b), $La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$(c) sintered at 1290^0C and $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$(d) sintered at 1250^0C.*

Hysteresis parameter	$LaFeO_3$	$La(Fe_{0,6}Ti_{0,4})O_3$	$La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$	$La(Fe_{0.4}Cu_{0.1}Ti_{0.6})O_3$
M_m(emu/g)	0,310	0,210	0,420	1,560
M_r (emu/g)	0,010	0,021	0,025	0,082
H_c (KOe)	5,7	18,2	5,3	0,15
$S = M_r / M_m$	0,032	0,10	0,06	0,05


LaFeO3
M [emu/g]
H [Oe]
0,4
0,2
0,0
-0,2
-0,4
-20000
-10000
0
10000
20000


La(Fe0,6Ti0,4)O3
M [emu/g]
H [Oe]
0,2
0,1
0,0
-0,1
-0,2
-20000
-10000
0
10000
20000

at 1250 °C




~ 10 µm

La(Fe0,3Co0,2Ti0,5)O3
M [emu/g]
H [Oe]
0,04
0,02
0,00
-0,02
-0,04
-20000
-10000
0
10000
20000

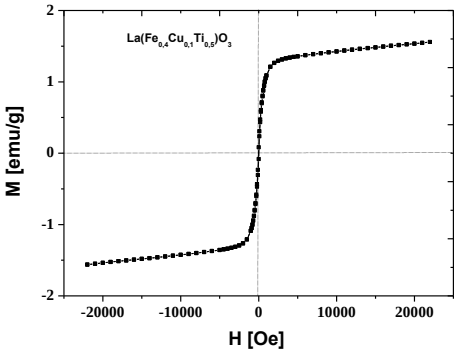

La(Fe0,4Cu0,1Ti0,5)O3
M [emu/g]
H [Oe]
2
1
0
-1
-2
-20000
-10000
0
10000
20000

Fig.5. *Magnetic hysteresis loops M(H) of $LaFeO_3$, $La(Fe_{0,6}Ti_{0,4})O_3$, $La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$ sintered at 1290^0C and $La(Fe_{0.4}Cu_{0,1}Ti_{0,5})O_3$ sintered at 1250^0C.*

Figure 8 is M(T) loop of $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ measured at H=100 Oe. Although the magnetic field is low (as in the case of Fig.6), it is enough to make the magnetization a high positive value at room temperature because ferromagnetism of the sample is stronger and the sample can be magnetized more easily. The Curie temperature of the sample $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ is about 450^0C.

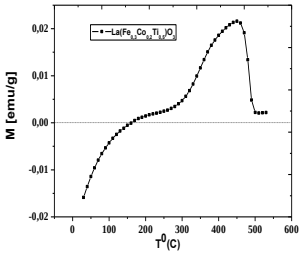


Fig. 6. *M(T) loop of $La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$ measured at magnetic field H=100Oe*

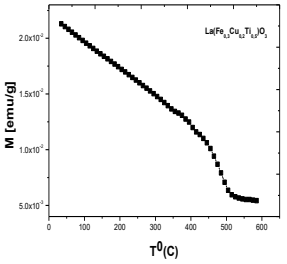


Fig. 7. *M(T) loop of $La(Fe_{0,3}Co_{0,2}Ti_{0,5})O_3$ measured at magnetic field H=1T*

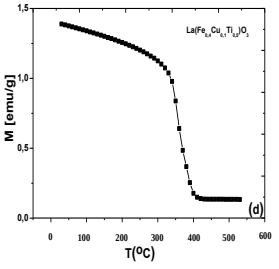


Fig. 8. *M(T) loop of $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ measured at magnetic field H=100Oe*

4. CONCLUSIONS

LaFeO3 system with Doped Ti, Co, Cu is manufactured successfully by using solid state reaction method. The manufactured samples have orthorhombic structure, theirs unit cell volumes increase once Ti, Co, Cu is doped into the sample. The crystal lattice deformation when doping is the main reason affecting the magnetic properties of samples. The size of the sample particles is quite homogeneous. The samples show ferromagnetic properties, among which **$La(Fe_{0.4}Cu_{0.1}Ti_{0,5})O_3$** shows the strongest ferromagnetic properties. Detecting extraordinary magnetizing phenomenon when measuring the M(T) loops of samples in small magnetic field.

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