Hue University Journal of Science: Natural Science; ISSN 1859–1388

Vol. 126, No. 1B, 2017, P. 139–144; DOI: 10.26459/hueuni-jns.v126i1B.4155

THERMOELECTRIC PROPERTIES OF $LaFeO_3$ SYSTEM DOPED WITH Ti, Co AND Cu

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Abstract: A $LaFeO_3$ system doped with Ti, Co, and Cu was manufactured using the solid-state reaction method. It was sintered at 1250 °C and 1290 °C for 10 hours with a heating rate of 3 °C/min. The materials have a single-phase and orthogonal-perovskite structure which is characteristic of the Pnma space group. The unit cell volume of the materials increases when Ti, Co, Cu replace Fe^{+3}. The size of the particles increases while raising the sintering temperature. The resistance depends on the temperatures between the room temperature and 1000 K. Doping Co, Cu with the nominal component $La(Fe_{0.2}Co_{0.2}Ti_{0.6})O_3$ and $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ increases the conductivity of materials. The Seebeck coefficient of $La(Fe_{0.6}Ti_{0.4})O_3$ changes from a positive value to a negative value at around 700 °C.

Keywords: $LaFeO_3$, doped with Ti, Co and Cu, conductivity, Seebeck coefficient

1 Introduction

The pevoskite material has the general form of ABO_3 with *A* being the cation of a rare earth element or an alkaline earth metal (Y, La, Nd, Sm, Ca, Ba, etc.) and *B* being the cation of a transition metal (Mn, Co, Fe). The replacement of different elements into the position of *A* or *B* or both can create a lot of change in the material. When perovskite materials are doped with other metal elements, their electric property is improved to suit different application purposes. Studies on the investigation and manufacture of perovskite materials have been made with familiar families of material such as $SrTiO_3$, $LaMnO_3$, $CaMnO_3$, and $LaFeO_3$ [1–7].

Previously, the thermoelectric ceramics team of the Section of Condensed Matter Physics, Department of Physics, University of Science, National University of Hanoi, have prepared $LaFeO_3$ doped with Ti, and it gives a very large positive Seebeck coefficient, about mV/K [8–9]. Although they have created a composite with a large positive Seebeck coefficient, the conductivity of the material (σ) is small and it is difficult to apply in practice. In this research, we try to improve the thermoelectric properties and the conductivity of the materials by doping Ti, Co, and Cu.

2 Experimental procedure

The sample $LaFeO_3$ doped with Ti, Co, Cu is manufactured by means of the solid-state reaction method: oxides La_2O_3 (99.5 %), Fe_2O_3 (99 %), Co_2O_3 (99 %), TiO_2 (99 %), and CuO (99 %) were

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Submitted: 22–5–2017; Revised: 14–6–2017; Accepted: 20–6–2017

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

The structure was investigated by means of X-ray diffraction using diffractometer D5005 which uses Kα radiation of the copper element, and the diffraction angle 2θ varied from 10 to 70° with each step of 0.02°. The model was smoothed, cleaned and covered with silver. The measurements of the temperature dependence of resistance (resistivity) were carried out in a range of temperatures from the room temperature up to 600 K with a Keithley–197A and self-recording system. The Four-Point-Probe Theory was used in this measurement along with a measurement processing software. The thermoelectric parameters were measured on the measuring system at the Institute of Applied Physics Academy of Science and Technology Vietnam. The particle size and morphology of the powder samples were investigated by means of SEM on the S–4800, Hitachi – Japan.

3 Results and discussions

The 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 the single phase of the orthogonal-perovskite structure which is characteristic of the Pnma space group.

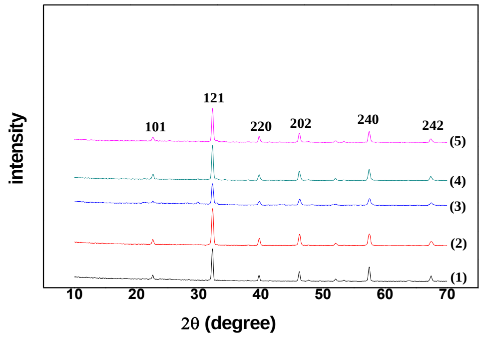

Fig. 1. X-ray diffraction diagram of samples sintered at 1290 °C: $LaFeO_3$ (1), $La(Fe_{0.6}Ti_{0.4})O_3$ (2), $La(Fe_{0.5}Ti_{0.5})O_3$ (3), $La(Fe_{0.4}Co_{0.1}Ti_{0.5})O_3$ (4) and $La(Fe_{0.3}Co_{0.2}Ti_{0.5})O_3$ (5)

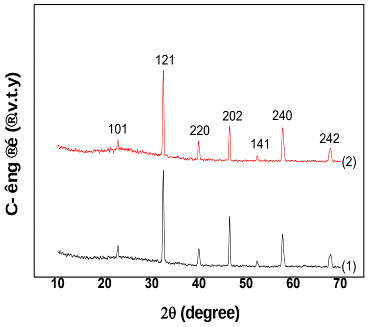

Fig. 2. X-ray diffraction diagram of $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ sintered at 1230 °C (1) and 1250 °C (2)

From the results of X-ray diffraction, the lattice parameters and unit cell volume of the samples were calculated and presented in Table 1 and Table 2. It can be seen from the data that the unit cell volume of the samples increases while replacing Fe^{+3} by Ti^{+4}, Co^{+3}, and Cu^{+2}. The reason is that the radius of Ti^{+4} (r = 0,650 Å), Co^{+3} (r = 0,648 Å), and Cu^{+2} (r = 0,730 Å) is larger than that of 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 thermoelectric properties of the samples.

Table 1. Lattice parameters, unit cell volume of sintered samples at 1290 °C

Compound	A (Å)	B (Å)	C (Å)	α	β	γ	V (Å)^3
$LaFeO_3$	5.570	5.532	7.890	90°	90°	90°	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 °C and 1250 °C

Temperature	A (Å)	B (Å)	C (Å)	α	β	γ	V (Å)^3
1230 °C	5.586	5.531	7.885	90^{o}	90^{o}	90^{o}	243.6
1250 °C	5.596	5.532	7.890	90^{o}	90^{o}	90^{o}	244.3

Figure 3 represents SEM images of Ti and Co-doped samples, sintered at 1290 °C. The size of the particles is quite homogeneous. Figure 4 shows SEM images of Ti and Cu doped samples, sintered at 1230 °C and 1250 °C. In the sample with CuO, whose fusion temperature is low, the diffusion process is enhanced by solid-state reactions with the presence of the liquid phase. The process of reaction is better and the particle size is larger, which leads to the increase of the sample density. From Figure 4, it can be seen that the particles are practically single crystals.

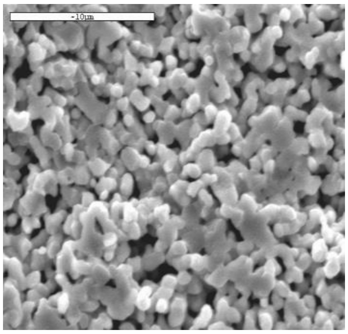

Fig. 3. a. SEM image of $LaFeO_3$ sintered at 1290 °C

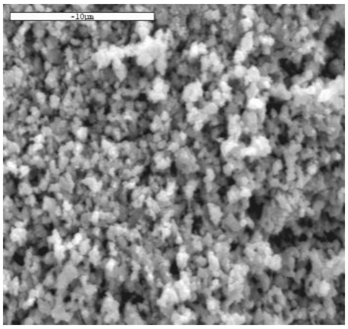

Fig. 3.b. SEM image of $La(Fe_{0.6}Ti_{0.4})O_3$ sintered at 1290 °C

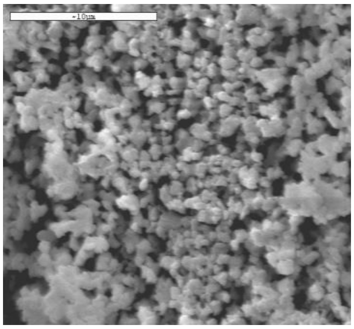

Fig. 3. c. SEM image of $La(Fe_{0.3}Co_{0.2}Ti_{0.5})O_3$ sintered at 1290 °C

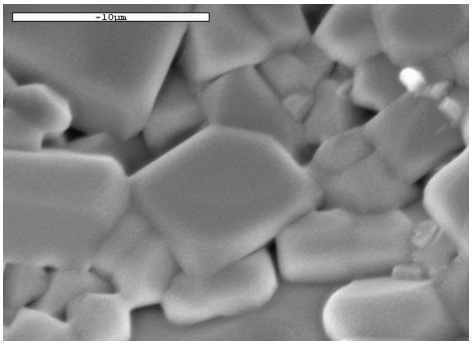

Fig. 4. a. SEM image of La($Fe_{0.4}Cu_{0.1}Ti_{0.5}$)O_3 sintered at 1230 °C

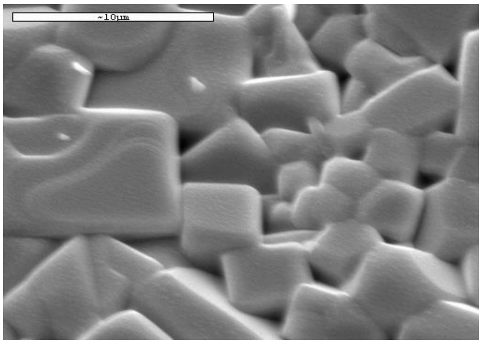

Fig. 4. b. SEM image of La($Fe_{0.4}Cu_{0.1}Ti_{0.5}$)O_3 sintered at 1250 °C

From Figure 5, the conductivity of the samples increases when doping Co and Cu with the nominal component La($Fe_{0.2}Co_{0.2}Ti_{0.6}$)O_3 and La($Fe_{0.4}Cu_{0.1}Ti_{0.5}$)O_3 (Figure 6). Among three samples, the conductivity of the Cu-doped sample increases most and reaches a peak at the temperature of 900 °C. Sample $LaFeO_3$ also demonstrates semiconducting properties based on 'hopping' mechanism of the ion pair Fe^{+3}–Fe^{+2} [10]. Both Co and Cu are able to have mixed valence Co^{+2}–Co^{+3} and Cu^{+1}–Cu^{+2} when they were sintered at high temperature and then cooled down to room temperature. Therefore, the mixed-valent state of ion pairs Fe^{+3}–Fe^{+2}, Co^{+3}–Co^{+2}, and Cu^{+2}–Cu^{+1} increases the conductivity of the materials. The conductive property of the materials is quite consistent with the small polaron jump model [11] (Fig. 7).

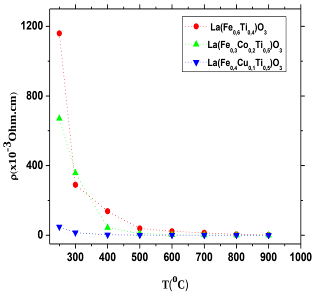

Fig. 5. Temperature dependence of resistivity ρ(T) of La(Fe0.6$Ti_{0.4}$)O_3, La($Fe_{0.3}Co_{0.2}Ti_{0.5}$)O_3 sintered at 1290 °C, and La($Fe_{0.4}Cu_{0.1}Ti_{0.5}$)O_3 sintered at 1250 °C

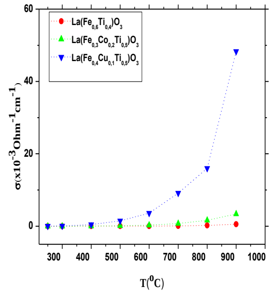

Fig. 6. Temperature dependence of conductivity of La($Fe_{0.6}Ti_{0.4}$)O_3, La($Fe_{0.3}Co_{0.2}Ti_{0.5}$)O_3 sintered at 1290 °C, and La($Fe_{0.4}Cu_{0.1}Ti_{0.5}$)O_3 sintered at 1250 °C

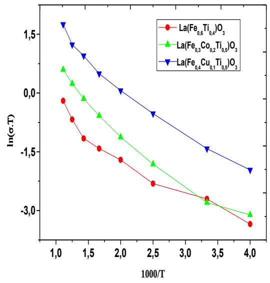

Fig. 7. Temperature dependence ln(σT)–1/T of La($Fe_{0.6}Ti_{0.4}$)O_3, La($Fe_{0.2}Co_{0.2}Ti_{0.6}$)O_3 sintered at 1290 °C, and La($Fe_{0.4}Cu_{0.1}Ti_{0.5}$)O_3 sintered at 1250 °C

$$\sigma = \frac{A}{T} exp\left(-\frac{E_a}{kT}\right)$$

where A is the temperature dependent constant T; k is the Boltzmann constant; E_a is the activation energy.

In a previous study [9], when Ti is doped into $LaFeO_3$, the compound has a high positive Seebeck coefficient but small conductivity. By doping Co and Cu to create $La(Fe_{0.2}Co_{0.2}Ti_{0.6})O_3$ and $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$, the conductivity increases, and $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ has the highest conductivity (Fig. 6).

The Seebeck coefficient and power factor were measured in the temperature range from room temperature to 1000 K and presented in Figure 8 and Figure 9. $La(Fe_{0.6}Ti_{0.4})O_3$ and $La(Fe_{0.3}Co_{0.2}Ti_{0.5})O_3$ have a positive Seebeck coefficient, while $La(Fe_{0.4}Cu_{0.1}Ti_{0.6})O_3$ has a negative one. WhenFe^{+3} is replaced by Ti^{+4}, Co^{+2}, and Cu^{+2} at the *B* position, the samples might appear as an n-type or p-type semiconductor, and the load might be a hole (p) or an electron (e) depending on the real valence and the number of ions. Especially, the Seebeck coefficient of $La(Fe_{0.6}Ti_{0.4})O_3$ can change from a positive value to a negative value at about 700 °C. This is because at high temperatures (> 700 °C in this case), electrons predominate and the material is an n-type semiconductor so S is less than 0 [12–15]. Despite its high positive Seebeck coefficient, the conductivity of $La(Fe_{0.6}Ti_{0.4})O_3$ is low, which leads to a low value of power factor. The power factor of $La(Fe_{0.3}Co_{0.2}Ti_{0.5})O_3$ and $La(Fe_{0.4}Cu_{0.1}Ti_{0.6})O_3$ increases (Fig.9). When the temperatures are greater or equal to 800 °C, the power factor of $La(Fe_{0.4}Cu_{0.1}Ti_{0.6})O_3$ is quite high (1.8.10^{-5} W^{-1}·K^{-2}).

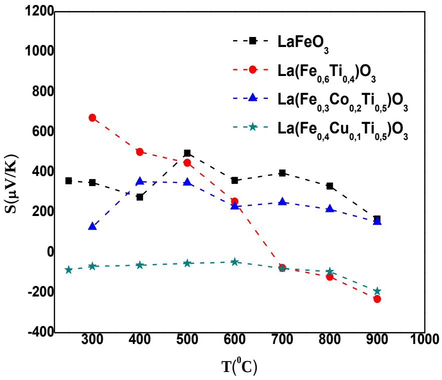

Fig. 8. Temperature dependence of Seebeck coefficient $La(Fe_{0.6}Ti_{0.4})O_3$, $La(Fe_{0.3}Co_{0.2}Ti_{0.5})O_3$ sintered at 1290 °C, and $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ sintered at 1250 °C

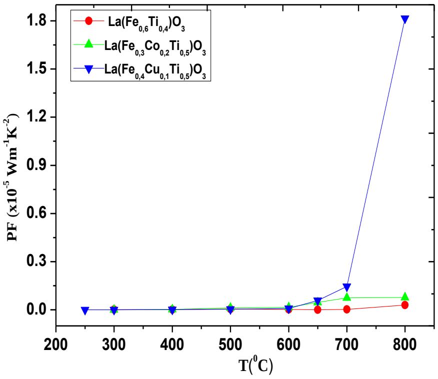

Fig. 9. Temperature dependence of power factor of $La(Fe_{0.6}Ti_{0.4})O_3$, $La(Fe_{0.3}Co_{0.2}Ti_{0.5})O_3$ sintered at 1290 °C, and $La(Fe_{0.4}Cu_{0.1}Ti_{0.5})O_3$ sintered at 1250 °C

4 Conclusions

The $LaFeO_3$ system doped with Ti, Co, Cu was manufactured successfully by using the solid-state reaction method. The manufactured materials have orthorhombic structure; their unit cell volumes increase when Ti, Co, Cu ions were doped into the sample. The crystal lattice deformation when doping is the main reason affecting the electric and thermoelectric properties of the samples. The size of the particles is quite homogeneous; the Cu- and Co-doped materials have high conductivity compared with the original material. The Seebeck coefficient of

$La(Fe_{0.6}Ti_{0.4})O_3$ can change from a positive value to negative value at about 700 °C. $La(Fe_{0.4}Cu_{01}Ti_{0.5})O_3$ has the highest power factor.

Acknowledgments: The author would like to thank Hue University for the financial support as a part of project No. DHH2016–03–82.

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