Effect of Sr-doped on thermal properties of nanoparticle (La, Sr)FeO$_3$

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Abstract. Structure and thermal properties of La$_{1-x}$Sr$_x$FeO$_3$ have been studied. (La, Sr)FeO$_3$ was synthesized by sol-gel method result in powder form. Structural study was carried out using X-Ray Diffraction (XRD) and TEM. XRD characterization for all samples show orthorhombic perovskite structure. The crystallite size of the materials lie in the range of 20-40 nm as calculated by using Schrerrer’s formula which is also supported by TEM images. The thermal properties were characterized by using DSC. DSC curves show increasing of Neel temperature with addition of Stronsium. Average specific heat capacity was also calculated.

1. Introduction

LaFeO$_3$, one of perovskite oxide, has been paid attention for many applications, such as cathode materials for fuel cells and alcohol sensor [1]. LaFeO$_3$ is antiferromagnetic material with Neel temperature of 740 K [2]. The A-site substituted LaFeO$_3$ can be used in various applications because their stable structure, high thermal stability, high dielectric constant, low dielectric loss, and high performances are significantly affected by the substitution [3]. Thermal properties of LaFeO$_3$ is dependent on crystallite size [1], in which crystallite size is also dependent on doped on A-site. However, the thermal properties study for this compound has not been well studied. Parida et al. [4] have measured the enthalpy and standard molar Gibbs energies of LaFeO$_3$ using high temperature Calvet micro calorimeter and solid oxide galvanic cell and found that -1334 kJ/mol and 128.9 J/mol.K, respectively.

In this work, we have synthesized (La, Sr)FeO$_3$ with $x = 0.0, 0.1, 0.2, 0.3$, and $0.4$ at.\% by sol-gel method to form material in nano-scale. We focused on the effect of Sr-doped on the structural and thermal properties of (La, Sr)FeO$_3$ nanoparticles materials.

2. Materials and methods

La$_{1-x}$Sr$_x$FeO$_3$ samples were prepared by sol-gel method. Briefly, La$_2$O$_3$ (Merck), Fe(NO$_3$)$_3$.9H$_2$O (Merck), Sr(NO$_3$)$_2$ (Merck), and citric acid were dissolved in 150 mL water. The resulting suspension was continuously stirred on a heating plate until it turned to a highly viscous gel. The gel was heated at 200°C until formed brown powder. Then, it was calcined at 900°C for 6 h. The phase identification was checked by using X-Ray Diffractometer (XRD) with Cu Kα ($\lambda = 1.54060$ Å) radiation in the 2θ range of 10°- 90° with a step size of 0.02°. Rietveld refinement of the diffraction pattern was carried out using the HighScore Plus software. The morphology of the samples was checked by TEM. Thermal properties of La$_{1-x}$Sr$_x$FeO$_3$ were characterized by DSC with range temperature of 30-500°C in nitrogen atmosphere.
3. Results and discussion

3.1. Structure analysis

Figure 1 shows XRD pattern of the nanoparticles of La$_{1-x}$Sr$_x$FeO$_3$ with $x = 0.1$, 0.2, 0.3, and 0.4 at.% at room temperature. High score plus software was employed to analyze all XRD pattern. All samples exhibit single phase orthorhombic perovskite structure. The refined structural parameters are tabulated in table 1. There are no significantly shifting in 2θ indicates that there are no significantly change in lattice parameters. Broadening peaks are also observed clearly by increasing of Sr concentration. As shown in the Table 1, the crystallite size decrease as Sr-doped is increased. It can be caused the ionic radii of Sr$^{2+}$ (144 pm) is larger than La$^{3+}$ (136 pm), then the substitution of Sr effected the oxidation of Fe$^{3+}$ ions to Fe$^{4+}$ ions. While the ionic radii of Fe$^{4+}$ (58.5 pm) is smaller than Fe$^{3+}$ (64.5 pm) that lead to the decrease of crystallite size [5].

![Figure 1. The XRD patterns of (La,Sr)FeO$_3$ nanoparticles calcined at 900°C for 6 h in air.](image)

**Table 1.** Refined lattice parameters and crystallite size of La$_{1-x}$Sr$_x$FeO$_3$ nanoparticles calcined at 900°C for 6 h in air.

| Samples | La$_{1-x}$Sr$_x$FeO$_3$ |  
|---------|------------------------|  
| x=0     | 5.5724 5.5558 5.5610 5.5575 5.5608 |  
| x=0.1   | 7.8765 7.8384 7.8499 7.8617 7.8676 |  
| x=0.2   | 5.5696 5.5434 5.5547 5.5275 5.4998 |  
| x=0.3   | 29.5 25.7 24.6 23.9 23.0 |  
| x=0.4   |  

Lattice parameters of La$_{1-x}$Sr$_x$FeO$_3$ (Å)

Crystallite size (nm)
3.2 TEM
The morphology and structure of La$_{1-x}$Sr$_x$FeO$_3$ nanoparticles were characterized by TEM, as shown in figure 2. The TEM characterization were prepared by placing microdrops of solution on a carbon film which supported by copper grid. It can be seen from figure 2 that the average particle size of the samples decreased with increasing of Sr-doping ((a) $x = 0.0$ and (b) $x = 0.4$) content which is consistent with XRD results.

3.3 Thermal analysis
Figure 3 shows DSC measurements of La$_{1-x}$Sr$_x$FeO$_3$ nanoparticles with $x = 0.0$, $0.3$ and $0.4$. The measurement were performed with heating rate of 10°C/min from 30°C to 500°C using 5 mg powder sample encapsulated in standard Al crucibles under nitrogen atmosphere. A phase transition which are Neel temperatures were observed at about 420°C in DSC curve of $x = 0.0$, 432°C of $x = 0.3$, and 435°C of $x = 0.4$. It can be seen that Neel temperature increases as Sr-doped increased. The similar phenomenon is found by Caranoni et al. [6] for double perovskite Pb$_2$ScTaO$_6$ and Pb$_2$ScNbO$_6$ at lower temperature. These mean antiferromagnetic phase spread in high temperature with increase of Sr-doped. The average specific heat ($C_p$) calculations were also analyzed using the corresponding DSC curves.

![Figure 2. TEM images of La$_{1-x}$Sr$_x$FeO$_3$ nanoparticles for the samples with (a) $x = 0.0$, (b) $x = 0.4$.](image)

![Figure 3. DSC curve of La$_{1-x}$Sr$_x$FeO$_3$ nanoparticles with $x = 0.0$, 0.3 and 0.4 between 30°C and 500°C with rate of 10°C/min in nitrogen atmosphere.](image)
Table 2. Average specific heat capacity ($C_p$) value calculation of La$_{1-x}$Sr$_x$FeO$_3$ nanoparticles with $x = 0.0, 0.1, 0.2, 0.3$ and $0.4$.

| $x$  | $C_p$ ($10^4$ J/g°C) |
|------|----------------------|
| 0.0  | 4.2                  |
| 0.1  | 4.3                  |
| 0.2  | 4.4                  |
| 0.3  | 6.8                  |
| 0.4  | 6.9                  |

Table 2 shows average specific heat capacity ($C_p$) value nanoparticles La$_{1-x}$Sr$_x$FeO$_3$ with $x = 0.0, 0.1, 0.2, 0.3,$ and $0.4$. The heat capacity was calculated from 300°C to 400°C. These results show that specific heat capacity of La$_{1-x}$Sr$_x$FeO$_3$ increase with the increasing of Sr-doped. Maximum value of specific heat capacity was found at $x = 0.4$.

4. Conclusions
La$_{1-x}$Sr$_x$FeO$_3$ with $x = 0.0, 0.1, 0.2, 0.3,$ and $0.4$ at.% nanoparticles has been successfully synthesized by sol-gel method. XRD characterization for all samples shows single phase orthorhombic perovskite structure. DSC curve shows the Neel temperature increases as Sr-doped increased.

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