Structural and morphological of Cu doped La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ perovskite

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Abstract. The structure and morphology of Cu doped perovskite La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ ($x=0$ and $x=0.05$) obtained by doping Cu on Mn sites have been studied. The material has been synthesized by using a sol-gel method. Material La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.95}$Cu$_{0.05}$O$_3$ ($x = 0$ and $0.05$) was characterized by XRD and Rietveld refinement, the crystal structure of both materials was hexagonal, and the cell volume was increased by the increment of the doping level. Characterization by SEM shows that the material has high homogeneity with larger crystallite average size when doped by Cu. By using point analysis of EDX characterization, it is confirmed that Cu ions have been successfully substituted. The composition of the material by using EDX does not make much difference from the calculation so that it can be inferred a good compositional purity.

1. Introduction

Perovskite manganites La$_{1-x}$A$_x$MnO$_3$ (A is a divalent ion, e.g., Ca, Sr, or Ba) have attracted much attention due to their potential applications in magnetic sensors and magnetic recording devices [1,2]. Electron transport in this material influenced by ion doped at A site [3,4]. Ion doped caused lattice distortion and enhancement of double exchange interaction [3,4].

In manganites, it is possible to doped at both La-site and Mn-site, much research has been done on the substitution at the La-site with rare earth, which can modify the Mn$^{3+}$-O$_2^-$-Mn$^{4+}$ network and in turn will intensively affect the intrinsic physical properties such as ferromagnetism. The substitution at the Mn site in perovskite oxides, with other transition metal ions[5] is more important because it not only modifies the Mn$^{3+}$-O$_2^-$-Mn$^{4+}$ network but also brings about much new exchange interaction between the Mn ion and the doped transition metal ions [5].

In this work, we observed the effect of Cu doping on the structure and surface morphology of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ ($x = 0$ and $0.05$). It is expected that Cu doping would affect the structure and morphology of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$.

2. Methods

The La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ samples with $x = 0.0$ and $0.05$ were prepared using sol-gel method. High purity La$_2$O$_3$, Ba(NO$_3$)$_2$, Sr(NO$_3$)$_2$, Mn(NO$_3$)$_2$, Cu(NO$_3$)$_2$ were dissolved in nitric acid and mixed them became one solution. Then followed by addition of a suitable amount of citric acid. Ammonia solution was added to adjust the pH. The solution then stirred at 353 – 363 K until the gel was formed. The dried gel was obtained by heated the sample at 397 K for 4 h. The dried gel was calcined at 773K for 5 h until it became a powder sample. The powder was compacted and sintered at...
1273 K for 12 h. X-Ray Diffraction characterization was used to investigate the crystal structure and lattice parameters of each sample. Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray were used to determine the surface morphology and compositional purity of these samples.

3. Results and Discussion

The XRD pattern of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ ($x = 0$ and $x = 0.05$) samples is shown in Figure 1. The structure of the sample did not change with increasing doping level. All diffracted peaks are remaining the same and well indexed corresponded to the hexagonal LaMnO3 structure. Unit cell volume and lattice parameter increase but lattice parameter c decrease with increasing Cu content. This result was also observed by Z. Liu et al.[6]. The result of Rietveld analysis to the XRD data was summarized in Table 1. The crystallite size was determined by Scherrer’s equation [7]. Hence, the crystallite size increases with an increase in the content of Cu.

Rietveld refinement analysis confirmed that all samples have a hexagonal structure and R-3c space group. The Mn site doping causes a change in the Mn$^{3+}$/Mn$^{4+}$ ratio and the exchange interaction between Mn$^{3+}$ and Mn$^{4+}$ pairs[8]. The mismatch of ionic radius between the dopant and Mn ions affects the crystal structure and lattice parameters. The ionic radius of Cu$^{2+}$ (0.73 Å) is larger than Mn$^{3+}$ (0.654 Å), and Mn$^{4+}$ (0.53 Å) and therefore the unit cell volume is found to increase [9].

![Figure 1.XRD pattern of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$MnO$_3$ and La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.95}$Cu$_{0.05}$O$_3$](image)

| Space group | La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$MnO$_3$ | La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{0.95}$Cu$_{0.05}$O$_3$ |
|-------------|----------------------------------|----------------------------------|
| Crystal structure | Hexagonal | Hexagonal |
| a [Å] | 5.512 | 5.521 |
| b [Å] | 5.512 | 5.521 |
| c [Å] | 13.43 | 13.42 |
| Volume [Å$^3$] | 408.14 | 409.06 |
| Crystallite size [nm] | 37.28 | 41.98 |
| Mn-O bond length[Å] | 1.965 | 1.962 |
| Mn-O-MnAngle [deg] | 163.84 | 166.1 |
| GoF | 1.054 | 1.28 |
| $R_{wp}$ (%) | 8.57 | 9.17 |
| $R_p$ (%) | 6.7 | 7.02 |
SEM images of $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.0$ and 0.05) samples are presented in Figure 2. It can be seen a change in the mean grain size of the samples. The mean grain size was determined using SEM images by calculating the minimum and the maximum dimension of a large number of particles. The calculated value of the mean grain size of the samples with $x = 0$ and $x = 0.05$ were 165.25 nm and 183.92 nm. From the value, it can conclude that the mean grain size of the particle increases when the composition of Cu increases. The mean grain size was in line with the crystallite size of the particles.

Figure 3 shows EDX analysis spectrum of $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.00$ and 0.05) samples. Identification by EDX analysis in each spectrum indicated that only constituent elements in $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ were identified which are La, Ba, Sr, Mn, Cu and O atoms. It is concluded that the sample has compositional purity. Table 2 demonstrated the compositional analysis of these samples. There is a slight difference between designated composition and measured one might be due to the EDX method is based on a semi-quantitative analysis. Hence, the results are not absolute.

![Figure 2: SEM images of (a) $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{MnO}_3$ (b) $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{0.85}\text{Cu}_{0.15}\text{O}_3$](image1)

![Figure 3: The measurement result of $\text{La}_{0.7}\text{Ba}_{0.1}\text{Sr}_{0.2}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ ($x = 0.0$ and 0.05)](image2)
Table 2 Compositional analysis of La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ (x = 0.0 and 0.05)

| Doping Concentration | Element composition | Designated Composition (at.%) | Measured Composition (at.%) |
|----------------------|---------------------|--------------------------------|-----------------------------|
| X = 0                | La                  | 14                             | 12.37                       |
|                      | Ba                  | 2                              | 1.22                        |
|                      | Sr                  | 4                              | 3.65                        |
|                      | Mn                  | 20                             | 16.64                       |
|                      | Cu                  | 0                              | 0                           |
|                      | O                   | 60                             | 66.12                       |
| X = 0.05             | La                  | 14                             | 13.07                       |
|                      | Ba                  | 2                              | 1.28                        |
|                      | Sr                  | 4                              | 3.33                        |
|                      | Mn                  | 19                             | 15.49                       |
|                      | Cu                  | 1                              | 0.69                        |
|                      | O                   | 60                             | 66.14                       |

4. Conclusion
La$_{0.7}$Ba$_{0.1}$Sr$_{0.2}$Mn$_{1-x}$Cu$_x$O$_3$ samples with x = 0.0 and 0.05 were successfully synthesized by using sol-gel method. The XRD patterns showed a hexagonal structure with R-3C space group. The effect of Cu$^{2+}$ doping did not change the structure of the material but increased the lattice parameters and volume unit cells. SEM characterization confirmed the main grain size of the material increased with increased the level of Cu. The materials have a homogeneity microstructure and a good compositional purity based on EDX characterization.

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