Study of structure and composition on
La$_{0.7}$Ba$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_y$ (x = 0, 0.03, 0.05 and 0.07)
prepared by sol-gel method

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Abstract. In this work, we have investigated the effect of Cu substitution on structural and chemical composition of La$_{0.7}$Ba$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_y$ (x = 0, 0.03, 0.05 and 0.07) synthesized by sol-gel method. The samples were sintered at 700 $^\circ$C for 24 hours. Analysis of X-Ray Diffractometer (XRD) patterns revealed that the samples are in cubic structure with space group Pm-3m. The result of Rietveld refinements showed that the increasing Cu doping influences the lattice parameter, unit cell volume and $d_{\text{average}}$. Goldschmidt’s tolerance factor was calculated and confirmed that cubic is the most stable structure. The average crystallite size ($D$) was determined by applying the Scherrer’s equation, indicating the sample in nanocrystalline. Their crystallite sizes are 17.9981, 18.5809, 15.9273 and 16.9486 nm for $x = 0, 0.03, 0.05$, and 0.07, respectively. The X-Ray Fluorescence (XRF) revealed a spectrum of Cu which means Cu has successfully substituted the Mn site. There is no significant difference between the designated and measured composition.

1. Introduction

Mixed valance perovskite manganites have a general formula of $RE_{1-x}AM_nTMO_{3}$, where $RE$ represents a trivalent rare earth ion (La, Nd, Pr and others), $A$ stands for a divalent alkaline earth ion (Ca, Sr and Ba) and $TM$ stands for transition metal (Cu, Ni, and Fe). They became the topic of a viable experiment, in the consequence of their attracting physical properties at circa the ferromagnetic (FM)–paramagnetic (PM) transition temperature (Curie temperature, transition metal-insulator temperature), namely the colossal magnetoresistance (CMR), magnetocaloric effects (MCE) (concerning to the magnetic entropy change) as well as the intense relation between structural and magnetic properties [1–8]. Doping of divalent alkaline earth at the La site introduces the mixed valances of Mn$^{2+}$ and Mn$^{4+}$ that was elaborated in the structure of Zener’s double exchange (DE) interaction [9]. Furthermore, the Mn-O-Mn bond angle and the Mn-O bond length, which are likewise related to the average ionic radius of the A-site, imply to physical properties of these manganites. The substitution at the Mn-site by other transition metal ions is also crucial because it does not simply modify the Mn$^{2+}$-O-Mn bond angle and the Mn-O bond length, which are likewise related to the average ionic radius of the A-site, imply to physical properties of these manganites. The substitution at the Mn-site by other transition metal ions is also crucial because it does not simply modify the Mn$^{2+}$-O-Mn bond angle and the Mn-O bond length, which are likewise related to the average ionic radius of the A-site, imply to physical properties of these manganites. However, generates several new interaction exchange between the Mn ion and the doped transition metal ions as well [1–8].

On the contrary, the preparation method highly influences the physical and chemical properties of...
the rare-earth perovskite materials. The sol-gel synthesis has become an interesting method to generate an exceptionally pure and crystalline oxide powders. This method has been used successfully to provide some benefits, namely better homogeneities, lower processing temperatures, short annealing times, high purity of materials and improved material properties [1,11].

In this work, we synthesize the nanocrystalline sample La$_{1-x}$Ba$_x$Nd$_{0.25}$Mn$_{0.75}$CuO$_x$ by sol-gel method. Parental compound La$_{1-x}$Ba$_x$Nd$_{0.25}$MnO$_x$ has been studied by Unlül et al. [8] showed $T_c$ near room temperature which makes the sample a good candidate for CMR and MCE. Because the radius of Cu ions (Cu$^{2+} = 0.73$ Å, Cu$^{4+} = 0.54$ Å) is close to that of Mn ions (Mn$^{2+} = 0.645$ Å, Mn$^{4+} = 0.53$ Å), the Mn-site can be occupied by Cu ions [1–7]. In this work, we conscientiously examine the influence of Cu-doping at Mn-site in the nanocrystalline La$_{1-x}$Ba$_x$Nd$_{0.25}$MnO$_x$ $(x = 0, 0.03, 0.05, 0.07)$ on structural and chemical composition because Cu substitution in mixed valance perovskite manganites has attracted tunable MCE and CMR [2,3]. Meanwhile, further physical properties investigation will be next work of our project.

2. Experimental

Nanocrystalline La$_{1-x}$Ba$_x$Nd$_{0.25}$Mn$_{0.75}$CuO$_x$ (LBNMCO) were prepared by sol-gel citrate-nitrate auto combustion method. The precursors used were La$_2$O$_3$ (Aldrich, 99.5%), Nd$_2$O$_3$ (Aldrich, 99.5%), Ba(NO$_3$)$_2$ (Merck, 99%), Mn(NO$_3$)$_2$.4H$_2$O (Merck, 98.5%), Cu(NO$_3$)$_2$.3H$_2$O (Merck, 99.5%), and citric acid C$_6$H$_{12}$O$_7$.H$_2$O (Merck 99.5%). Stoichiometric amounts of greatly purified metal nitrates were dissolved together in a minimum amount of aquabidest water to obtain a clear solution [11]. We used the precursors in metal nitrate meanwhile oxide metal precursors were diluted by nitrate acid. After each precursor has become a clear solution, the precursor was mixed to synthesize La$_{1-x}$Ba$_x$Nd$_{0.25}$Mn$_{0.75}$CuO$_x$ perovskite sample according to the reaction:

$$0.7\text{La(NO}_3)_3 + 0.25\text{Ba(NO}_3)_2 + 0.05\text{Nd(NO}_3)_2 + (1-x)\text{Mn(NO}_3)_2.4\text{H}_2 \quad \text{(1)}$$

$$+ x\text{Cu(NO}_3)_2.3\text{H}_2\text{O} + \beta \text{C}_6\text{H}_8\text{O}_7.\text{H}_2\text{O}$$

$$\rightarrow \text{La}_{0.7}\text{Ba}_{0.25}\text{Nd}_{0.05}\text{Mn}_{1-x}\text{Cu}_x\text{O}_3 + \delta\text{N}_2 + \gamma\text{H}_2\text{O} + \alpha$$

Citric acid was mixed with the metal nitrates solution. Citric acid carries double functions, serving as the metal ion’s complexant as well as the fuel [12]. The solution was stirred continuously and heated up to 80 °C on a magnetic hot plate stirrer. The sample was calcinated at 600 °C for 6 hours to eliminate the organic substance, and then powder LBNMCO was sintered at 700 °C for 24 hours. Crystal structure and phase purity of samples were determined using X-ray diffractometer at room temperature. The chemical composition of samples was characterized using X-ray fluorescence.

3. Results and discussion

The crystal structure of LBNMCO series was characterized by XRD. Figure 1 shows the same XRD patterns for each sample. However, there is an indication of the presence of another peak emerging beside the peak of lanthanum manganite at Cu doped with concentration $x = 0.07$. The peak is from La$_2$O$_3$, which appears as the secondary phase. The peak appears because of sintering process at low temperature. The mixed valance perovskite manganite, the structure for doped lanthanum manganite phase begins to form crystallization above 700 °C [12].
Figure 2. Rietveld analysis result from sample La$_{0.7}$Ba$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_3$ for (a) $x=0$, (b) $x=0.03$, (c) $x=0.05$ and (d) $x=0.07$ sintered at 700°C.

Figure 3. Structure La$_{0.7}$Ba$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_3$.

The diffraction pattern of LBNMCO series has been refined using Rietveld analysis as shown in figure 2. The refinement’s product indicated that all samples are cubic structure with space group Pm-3m such as figure 3. The substitution of Cu ions for Mn-site does not change the lattice parameters significantly. The structure stability was confirmed by Goldschmidt’s tolerance factor ($\tau$). The value of $\tau$ can be determined by using the formulation:

$$\tau = \frac{<r_A>+r_\theta}{\sqrt{2}(<r_B>+r_\theta)}$$  \hspace{1cm} (2)

with $r_A$, $r_B$, and $r_\theta$ being ionic radii of each element on A-site (La$^{3+}$, Nd$^{3+}$, and Ba$^{2+}$), $r_B$ is ionic radii of the B-site (Mn$^{3+}$ and Cu$^{3+}$), and $r_\theta$ is ionic radii of O$^2-$. The stable manganite perovskite structure possesses a $\tau$ factor which is
that Cu successfully substituted and closed for the calculated concentration. XRF meas

Figure 4 and the concentration of the calculated result of average crystallite size in the range of 15–19 nm.

The average crystal structure is calculated using Scherrer formula as follow:

\[ D = \frac{0.9 \lambda}{\beta_{HKL} \cos \theta} \]  

(3)

where \( D \) is crystallite size, \( \lambda \) is Cu-K\( \alpha \) radiation which is used during XRD measurement (1.5406 Å), \( \beta_{HKL} \) is full-width at half maximum (FWHM) of each diffraction peak in radian unit, and \( \cos \theta \) is value of each diffraction position peak. The calculated result of average crystallite size in the range of 15–19 nm. The low sintering temperature resulted in nanocrystalline sample [12].

The XRF characterization was used to confirm what elements are contained in the material LB0.7Ba0.25Nd0.05MnO3 and confirmed that Cu substitution is successful. XRF measurement results can be seen in figure 4 and the concentration of the contained elements can be seen in table 2. Spectrum Cu confirms that Cu successfully substituted and closed for the calculated concentration.

Table 1. Structural parameter from Rietveld analysis for La\(_x\)Ba\(_{0.7}\)Nd\(_{0.25}\)Mn\(_{1-x}\)Cu\(_3\)O.

| Parameter                        | La\(_x\)Ba\(_{0.7}\)Nd\(_{0.25}\)Mn\(_{1-x}\)Cu\(_3\)O |
|----------------------------------|--------------------------------------------------|
| Structure                        | cubic                                            |
| Space Group                      | cubic                                            |
| \( a = b = c \) (Å)              | 3.9020                                           |
| Volume Unit Cell (Å\(^3\))       | 59.4096                                          |
| \( d_{	ext{av}} \) (Å)           | 1.9510                                           |
| <Mn-O-Mn> (degrees)              | 180                                              |
| Average Crystallites size (nm)   | 17.9981                                          |
| Goldschmidt’s tolerance factor (\( \tau \)) | 0.97972                                          |
| discrepancy factor GoF           | 1.1807                                           |
| RwP                              | 6.6129                                           |
| RP                               | 5.2261                                           |

in the range \( 0.89 < \tau < 1.02 \). The calculation results \( \tau \) are close to 1 summarized in table 1, which belongs to cubic structure [10]. As reported by Ünlü et al. [8] that in the parental compound La0.7Ba0.25Nd0.05MnO3 has a cubic structure.

Table 1 shows the lattice parameter result of Rietveld refinement. The effect of Cu substitution change lattice parameters, unit cell volume, and average Mn-O bond length. Because, it has a cubic structure, the angle of Mn-O-Mn is 180°. For \( x = 0.02 \) and \( x = 0.05 \) lattice parameters, unit cell volume, and average Mn-O bond length decreased but increased at \( x = 0.07 \). It indicates that there is a difference in the percentage of substituted Cu ions. Accordingly, the observed lattice parameter in samples can be defined in terms of the differences in the ionic radii and the variations in the percentages of the Cu\(^{2+}\) and Cu\(^{4+}\) ions with an increase in Cu doping level [1]. Several XPS study reported that substitution of Cu ions on the Mn-site showed Cu ions existed in the form of mixed Cu\(^{2+}\) and Cu\(^{4+}\) [1-7].

The B-site (six-coordinated) ionic radius of Cu\(^{2+}\) (0.73 Å) is greater compared to Mn\(^{4+}\) (0.645 Å) and the ionic radius of Cu\(^{4+}\) (0.54 Å) is close to that of Mn\(^{3+}\) (0.53 Å) and smaller compared to the radius of the high spin state of Mn\(^{4+}\) (0.645 Å) [5]. Ghosh et al. [6] reported that average radii of Mn\(^{4+}\) and Mn\(^{2+}\) at lanthanum manganite that is doped on La-site about \( x = 0.3 \) (La,Sr,MnO) are estimated to be 0.619 Å. A smaller ion at the doped site on the subject neighboring Mn–O bonds to centric push reduces the Mn–O bond length. A larger ion at the doped site can subject the neighboring Mn-O bonds to a centric pull and creating an increase in the Mn–O length [4]. The Cu\(^{4+}\) (0.54 Å) which is smaller compared to the R(Mn\(_x\)) stretches the to centric pull generating a reduction in the Mn–O bond [4,5]. Therefore, one can expect that Cu ions presents in the form of Cu\(^{4+}\) dominant at Mn-sites for \( x = 0.03 \) and \( x = 0.05 \) whereas Cu\(^{2+}\) dominant for \( x = 0.07 \).
Table 2. The XRF result sample La$_{0.7}$Ba$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_3$ compared to calculation based on the stoichiometry process.

| Element | Calculated (%) | Measured (%) |
|---------|---------------|--------------|
|         | 0  | 0.03 | 0.05 | 0.07 | 0     | 0.03 | 0.05 | 0.07 |
| La      | 53.63 | 53.56 | 53.51 | 53.46 | 54.35 | 53.79 | 54.09 | 54.21 |
| Ba      | 12.08 | 12.07 | 12.05 | 12.04 | 14.03 | 15.09 | 14.26 | 13.91 |
| Nd      | 3.98  | 3.97  | 3.97  | 3.97  | 3.46  | 3.63  | 3.63  | 3.72  |
| Mn      | 30.30 | 29.35 | 28.72 | 28.09 | 34.63 | 36.34 | 36.34 | 37.2 |
| Cu      | 0     | 1.05  | 1.75  | 2.45  | 0.00  | 1.15  | 1.96  | 2.70  |
| Total   | 100   | 100   | 100   | 100   | 100   | 100   | 100   | 100   |

Figure 4. XRF result reveals that three different samples of La$_{0.7}$Ba$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_3$ sintered at different temperature produce the same spectrum without any sign of impurities.

4. Conclusions

The La$_{0.7}$Ba$_{0.25}$Nd$_{0.05}$Mn$_{1-x}$Cu$_x$O$_3$ ($x = 0, 0.03, 0.05, 0.07$) material has been successfully prepared by applying the sol-gel method. X-ray diffraction (XRD) characterization results show that samples are cubic structure with space group Pm-3m. Goldschmidt’s tolerance factor was calculated and confirmed that cubic is the most stable structure. The effect of Cu substitution changes lattice parameters, unit cell volume, and average Mn-O bond length. The Cu ions exists in the form of Cu$^{3+}$ dominant at Mn sites for Cu ion concentration $x = 0.03$ and $x = 0.05$, whereas Cu$^{2+}$ dominant for $x = 0.07$. The average crystallite size ($D$) was specified by applying the Scherrer’s equation, indicating the sample in nanocrystalline. The X-Ray Fluorescence (XRF) reveal spectrum of Cu that means Cu has successfully substituted the Mn site.

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