Effect of Ca-Doping on the Structure and Morphology of Polycrystalline La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ ($x =$ 0; 0.03; and 0.05)

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Abstract. In this paper, we report structure and morphology of polycrystalline La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ ($x =$ 0; 0.03; 0.05). Basically, these materials are perovskite manganites type with the general structure $A$MnO$_3$ ($A =$ trivalent rare earth with divalent ion-doped) which have been extensively studied due to their interesting physical properties. It was known that the electron transport in this material influenced by ion doped at $A$ site. Doping with different divalent ions should cause the lattice distortion. Hence, double exchange interaction is enhanced. In this study, we prepared our sample through the sol-gel method. It is show that the method has resulted in powder materials with ultra-fine particle size. The effect of Ca$^{+2}$ and Ba$^{+2}$ doping on the structure did not make any phase changing, but the lattice parameter of La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ decreased below $x =$ 0.03. Microstructure observed by scanning electron microscope to the sintered samples indicated that the microstructure is homogeneous with fine size of equiaxed grain morphology. Microanalysis by EDS confirmed there is no significant different between designated composition and measured one. It is concluded that effect of Ca$^{+2}$ and Ba$^{+2}$ doped in LaMnO$_3$ has resulted in microstructural and lattice parameter changes. The doped materials are remaining single phase.

1. Introduction
Manganites with perovskite structure has the general formula $A$MnO$_3$ ($A =$ trivalent rare earth with divalent ion-doped) [1-3]. The material has been extensively studied due to their interested physical properties [1-4]. Electron transport in this material influenced by ion doped at $A$ site [2,3]. Ion doped caused lattice distortion and enhancement double exchange interaction [2,3]. Hence, it would influence transport properties in the material.

Transport properties in polycrystalline material can be explained by a core-shell model [5-7]. Each particle consists of core and shell [5-7]. Double exchange (DE) interaction is very crucial factor that influence the transport properties of the material. DE interaction is electron simultaneously hopping from Mn$^{3+}$ ion to Mn$^{4+}$ ion via O$^{2-}$ ion [1]. The interaction dominant in the core. Hence promotes ferromagnetic behavior in this part. And the other shell is one part where the occurrence insulates region near the grain boundaries. Since this part consist of vacancies, defects, stress, and broken bonds, which causes decrement of DE interaction [5,7]. Intergrain distance plays an important role in the electron transport in a polycrystalline material [6]. When the intergrain distance becomes larger, electron transport becomes more difficult [6]. The consequence is the resistivity of the samples will decrease [6].

Preparation material by sol-gel method has been an interested study of the obtained material which has distribution of homogeneous size and improve physical properties of the material [9]. In this work,
we observed the effect Ca-doping on the structure and surface morphology of polycrystalline La$_{0.7}$Ba$_{0.3}$MnO$_3$ ($x = 0; 0.03; 0.05$). It is expected that Ca-doping would influence structure and morphology of La$_{0.7}$Ba$_{0.3}$MnO$_3$ and by using core-shell model we can explain transport properties of La$_{0.7}$Ba$_{0.3}$MnO$_3$. Ca-doping was chosen because it can reduce Curie temperature ($T_c$) of La$_{0.7}$Ba$_{0.3}$MnO$_3$. It is important due to La$_{0.7}$Ba$_{0.3}$MnO$_3$ is one of candidate for application since the material has high magnetoresistance and magnetocaloric properties [2,3].

2. Experiment Method

Polycrystalline La$_{0.7}$ (Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ ($x = 0; 0.03; 0.05$) were fabricated by the sol-gel method. The precursors were La$_2$O$_3$ (Merck, 99.5%), BaCO$_3$ (Merck, 99%), CaCO$_3$ (Merck, 99.0%), and Mn(NO$_3$)$_2$·4H$_2$O (Merck, 98.5%). Stoichiometric amounts of each precursor were dissolved in nitric acid and then mixed them become one solution. After that, citric acid (Merck, 99%) was added to the solution with a molar ratio of citric acid/total metal ions being 1.0. Ammonia solution was used to adjust the pH value of the solution to 7. Stirred the solution at 353 K - 363 K until gel was formed. The gel was heated at 393 K for 4 hours in the dehydration process until the dried gel was obtained. After dehydration process, dried gel was heated at 873 K for 8 hours and finally the resulting powder was heated at 1123 K for 10 hours. The obtained powder was compacted and then further sintered at 1573 K for 30 hours to further crystal growth and grains become closer packed.

The X-ray diffraction with Cu-Kα radiation (Shimadzu) was used to determine crystal structure and lattice parameters of each sample. Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX) was used to determine the surface morphology and compositional purity of these samples.

3. Results and Discussion

The XRD pattern of polycrystalline La$_{0.7}$ (Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ ($x = 0; 0.03; 0.05$) samples is shown in Figure 1. No structural changes occurring in the samples could be seen with increasing $x$ value where the patterns are remaining the same. All diffracted peaks are well indexed correspond to the rhombohedral LaMnO$_3$ structure.

![Figure 1. XRD patterns of polycrystalline La$_{0.7}$ (Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$](image)

Table 1. Refined structural parameters of polycrystalline La$_{0.7}$ (Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$

| Parameter structure | $x = 0$ | $x = 0.03$ | $x = 0.05$ |
|---------------------|--------|----------|----------|
| Space group         | R-3c   | R-3c     | R-3c     |
| Crystal structure   | Rhombohedral | Rhombohedral | Rhombohedral |
| a (Å)               | 5.5355 | 5.5464   | 5.5426   |
| b (Å)               | 5.5355 | 5.5464   | 5.5426   |
However, a small shift in peak position (in set of Fig. 1) as the x value increased can be seen indicating a change in lattice parameter. Results of Rietveld analysis to the XRD data were summarized in Table 1. Crystallite size of the material evaluated by XRD measurement using WPPM method (Whole Powder Pattern Modelling). Crystallite size distribution of the material shows in Figure 2. The mean crystallite size of the material with x = 0, 0.03, and 0.05 were 46 nm, 47.3 nm, and 47.8 nm respectively. It is shown that there is slightly difference in crystallite size distribution due to increasing doping concentration. It is indicated that doping concentration until 5wt% did not affected to the distribution of crystallite size of the material.

![Figure 2](image)

**Figure 2.** The crystallite size cumulative distribution of polycrystalline La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$

Rietveld refinement analysis confirmed that all samples have rhombohedral structure and R-3c space group. It is evident that the increment of Ca concentration in polycrystalline La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ caused an increase in lattice parameters compared with un-doped sample. However, the length of the lattice axis for samples x = 0.03 and 0.05 is slightly different. The increase in lattice parameter of La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ samples is shown in Figure 3. These results are in good agreement with literature [2,3]. The increment of lattice parameters and unit cell volume due to Ca doping concentration might occur because the average ionic radius in A-site increase with increasing doping concentration [2,3].

![Figure 3](image)

**Figure 3.** Doping concentration dependent lattice parameter and unit cell volume of La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$

![Figure 4](image)

**Figure 4.** Doping concentration dependent Mn-O-Mn bond length of La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$
Figure 4 demonstrates doping concentration dependent to the Mn-O-Mn bond length. Mn-O bond length and Mn-O-Mn bond angle could get by Rietveld refinement analysis. The change of Mn-O-Mn bond length would impact the transport properties of polycrystalline $\text{La}_{0.7}\text{(Ba}_{1-x}\text{Ca}_x\text{)}_{0.3}\text{MnO}_3$. Since polycrystalline sample consist of grains with intergrain distance to be about $d/2$, where $d$ is Mn-O-Mn bond length [6]. Core-shell model of perovskite manganites depicts in Figure 5. When the intergrain distance becomes larger, electron transport becomes more difficult [6]. The consequence is the resistivity of the material will decrease [6]. It means that there is decrement of DE interaction due to the increment of Mn-O-Mn bond length [6]. The change of Mn-O-Mn bond length occurred because doping in $A$ site of perovskite structure caused lattice distortion [2,3].

![Figure 5. Core-shell model of perovskite manganites [6]](image)

SEM images of $\text{La}_{0.7}\text{(Ba}_{1-x}\text{Ca}_x\text{)}_{0.3}\text{MnO}_3$ ($x = 0; 0.03; 0.05$) samples are presented in Figure 6. The images showing close pack grains microstructure with equiaxed grain morphology randomly oriented. A change in mean grain size of the samples could be clearly seen in the images. The mean grain size of the samples with $x = 0, 0.03$, and $0.05$ were 274 nm, 229 nm and 1970 nm respectively. A significant increase occurred in sample with $x = 0.05$ but grains become more packed.

![Figure 6. SEM images of $\text{La}_{0.7}\text{(Ba}_{1-x}\text{Ca}_x\text{)}_{0.3}\text{MnO}_3$ samples (a) $x = 0$ (b) $x = 0.03$ (c) $x = 0.05$](image)

Figure 7 shows Energy Dispersive X-ray (EDX) analysis spectrum of $\text{La}_{0.7}\text{(Ba}_{1-x}\text{Ca}_x\text{)}_{0.3}\text{MnO}_3$ samples. Identification by EDX analysis in each spectrum indicated that only constituent elements in $\text{La}_{0.7}\text{(Ba}_{1-x}\text{Ca}_x\text{)}_{0.3}\text{MnO}_3$ were identified. It is concluded that the compositional purity of all samples is confirmed. Moreover, there is no quantifiable loss of each element during the sample preparation process. It was demonstrated in Table 2 which summarized the compositional analysis of these samples. A slight difference in quantitative value between designated composition and measured one might be due to the EDX method is based on semi quantitative analysis. Hence, the results are not absolute.

![Figure 7. The measurement result of EDX analysis of polycrystalline $\text{La}_{0.7}\text{(Ba}_{1-x}\text{Ca}_x\text{)}_{0.3}\text{MnO}_3$ (a) $x = 0$ (b) $x = 0.03$ (c) $x = 0.05$.](image)
Table 2. Compositional analysis of polycrystalline La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$

| Doping concentration | Element composition | Designated composition (at.%), measured composition (at.%) |
|----------------------|---------------------|------------------------------------------------------|
| $x = 0$              | La                  | 14.00, 13.36                                       |
|                      | Ba                  | 6.00, 5.70                                        |
|                      | Ca                  | 0.00, 0.00                                        |
|                      | Mn                  | 20.00, 17.14                                      |
|                      | O                   | 60.00, 63.80                                      |
| $x = 0.03$           | La                  | 14.00, 13.32                                       |
|                      | Ba                  | 5.82, 6.00                                        |
|                      | Ca                  | 0.18, 0.14                                        |
|                      | Mn                  | 20.00, 17.53                                      |
|                      | O                   | 60.00, 63.01                                      |
| $x = 0.05$           | La                  | 14.00, 11.83                                       |
|                      | Ba                  | 5.70, 4.80                                        |
|                      | Ca                  | 0.30, 0.24                                        |
|                      | Mn                  | 20.00, 15.75                                      |
|                      | O                   | 60.00, 67.38                                      |

4. Summary
The synthesis of polycrystalline La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ ($x = 0$; 0.03; 0.05) materials by the sol-gel method were successfully achieved. The effect of Ca$^{2+}$ and Ba$^{2+}$ doping on the structure did not make any phase changing, but the lattice parameter of La$_{0.7}$(Ba$_{1-x}$Ca$_x$)$_{0.3}$MnO$_3$ decreased below $x = 0.03$. Ca-doping in synthesized materials leads to the homogeneous microstructure with fine size of equiaxed grain morphology. By using core-shell model, we can conclude that such effects to the structure of the material would give impact to the transport properties of these materials.

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