Effects of Ag doping on the microstructural, morphological, and magnetic properties of a perovskite material, (La$_{1-x}$Ag$_x$)$_{0.3}$Ca$_{0.2}$MnO$_3$

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Abstract. In this study, perovskite (La$_x$Ag$_{1-x}$)$_{0.3}$Ca$_{0.2}$MnO$_3$ material was synthesized using the sol-gel method with different Ag doping levels ($x = 0.03$ and 0.1). The precursors, LaO, AgNO$_3$, Ca(NO$_3$)$_2$, Mn(NO$_3$)$_2$.4H$_2$O were combined stoichiometrically and sintered at 900°C for 24 h. Energy dispersive X-ray spectroscopy was used to confirm the purity of each sample. Rietveld refinement of the X-ray diffraction pattern showed that the samples had a single phase and orthorhombic structure with the Pnma space group. Scanning electron microscopy revealed density, porosity, and granular morphology that affected the characteristics of the sample. The magnetic hysteresis curves indicate that the material was paramagnetic and material with $x = 0.1$ has a higher magnetic susceptibility than with $x = 0.03$.

Keywords: perovskite, Ag-doping, sintering, sol-gel

1. Introduction

LnMnO$_3$ is one of fascinating material to study. This material is an antiferromagnetic (AFM) insulator with Neel temperature ($T_N$, the temperature above which the material becomes paramagnetic) around 140 K. The Ln site can be substituted with alkali element or alkali earth element (A) to form Ln.A,MnO$_3$ (where Ln is a trivalent rare earth element and A is alkaline elements or alkaline earth elements which shows unique physical properties around the phase transition temperatures ($T_C$) of paramagnetic (PM)–ferromagnetic (FM), including colossal magnetoresistance and magnetocaloric effects [1–4].

LCMO perovskite materials can be applied in the fields of, magnetic cooling, sensors, medicine, biology, medicine, catalysts and memory devices [5]. Changes its chemical composition and applying several treatments to the manganite perovskite material can modify the microstructure so that the nature of its physical characteristics of this material can be improved [6–7].

In this study, perovskite (La$_x$Ag$_{1-x}$)$_{0.3}$Ca$_{0.2}$MnO$_3$ material were synthesized by the sol-gel processes. Ag doping effects on structural, morphological, and magnetic properties of materials will be studied.

2. Experimental

(La$_x$Ag$_{1-x}$)$_{0.3}$Ca$_{0.2}$MnO$_3$ materials were prepared by the sol-gel method for $x = 0.03$ and 0.1. Precursors, LaO, AgNO$_3$, Ca(NO$_3$)$_2$.4H$_2$O, and Mn(NO$_3$)$_2$.4H$_2$O dissolved with nitric acid. Citric acid (C$_6$H$_8$O$_7$·H$_2$O) was added in a molar ratio of 1:1.2 for citric acid to metal ions in total. Adjustment of the pH solution until pH 7 is achieved by adding ammonia solution. Then the magnetic stirrer with a speed of 400 rpm was used to homogenize the mixture which was carried out at temperature of 80–90 °C.
Table 1. Lattice parameters and unit cell volumes of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ (x = 0.03 and 0.1)

| Samples                  | a (Å) | b (Å) | c (Å) | Volume (Å$^3$) |
|--------------------------|-------|-------|-------|----------------|
| (La$_{0.77}$Ag$_{0.03}$)$_{0.8}$Ca$_{0.2}$MnO$_3$ | 5.47081 | 7.73883 | 5.50146 | 232.919 |
| (La$_{0.7}$Ag$_{0.1}$)$_{0.8}$Ca$_{0.2}$MnO$_3$ | 5.50063 | 7.74575 | 5.47364 | 233.2125 |

Figure 1. XRD pattern of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ (x = 0.03 and 0.1)

Figure 2. SEM image of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ for (a) x = 0.03 and (b) x = 0.1

The resulting gel is then dried by heating it for 3 h at a temperature of 120 °C so that the gel becomes high viscosity. The decomposition of organic precursor was carried out on the high viscosity gas by calcining it for 5 h at 500 °C. Then proceed with sintering process for 24 h at 900 °C. Characterisation of the sample with X-ray diffraction (XRD) was done to identify phases and analyse sample structures. Scanning electron microscopy (SEM) was carried out to observe the morphology of the sample. Determination of the elemental composition contained in the sample was carried out by Energy Dispersive X-ray (EDX) spectroscopy. Finally, vibrating sample magnetometer (VSM) was used to obtain the M-H hysteresis curve of the samples.

3. Results and discussion

Refined results from the XRD pattern of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ and (La$_{0.7}$Ag$_{0.1}$)$_{0.8}$Ca$_{0.2}$MnO$_3$ material that indicate characteristic peaks of the sample compound, are shown in figure 1. At room temperature, the system shows the perovskite structure belonging to the Pnma space group in the orthorhombic crystal system.
Figure 3. EDX image of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ for (a) $x = 0.03$ and (b) $x = 0.1$

Figure 4. M-H loop showing the hysteresis of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ for $x = 0.03$ and $x = 0.1$

The unit cell volume and the lattice parameters of (La$_{0.77}$Ag$_{0.03}$)$_{0.8}$Ca$_{0.2}$MnO$_3$ material are shown in table 1. The values are smaller than (La$_{0.7}$Ag$_{0.1}$)$_{0.8}$Ca$_{0.2}$MnO$_3$ material. This is because the radius of the Ag$^+$ ion (1.28 Å) as a dopant is greater than La$^{3+}$ ion (1.22 Å).

Figure 2 shows the SEM patterns of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ when $x = 0.03$ and 0.1. Grain size increases with higher Ag doping levels. The (La$_{0.77}$Ag$_{0.03}$)$_{0.8}$Ca$_{0.2}$MnO$_3$ sample was found to have agglomerated particles. This is because of the increase in magnetic moments due to suppression of antiferromagnetic ordering in material [5].

Figure 3 shows the chemical composition and semi-quantitative EDX measurements results. There were no impurities present in both samples ($x = 0.03$ and 0.1). EDX also shows that there was no quantifiable loss of any elements.

The VSM characterization results of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ materials are shown in figure 4. The results show that the sample with $x = 0.03$ is paramagnetic because there was no Hc value. However, sample with $x = 0.1$ was found as soft magnetic with a magnetization value of 9 emu/g. The susceptibility of (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ when $x = 0.1$ is greater than $x = 0.03$ at room temperature. The hysteresis curves indicate that both samples are paramagnetic and that Ag doping with $x = 0.1$ produces a higher magnetic susceptibility than with $x = 0.03$.

4. **Summary**

In this study, (La$_{1-x}$Ag$_x$)$_{0.8}$Ca$_{0.2}$MnO$_3$ materials were synthesized by a sol-gel process with two different Ag doping levels ($x = 0.03$ and 0.1). The microstructure of the obtained perovskite materials has more favorable characteristics on doping with $x = 0.1$. The results of SEM and EDX indicate that the
characteristics of the sample were likely derived from density, porosity, and granular morphology. Moreover, grain sizes increases with higher Ag-doping levels.

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