

Effect of Temperature and Duration of Sintering on Perovskite Material $(\text{La}_{1-x}\text{Ag}_x)_{0.8}\text{Ca}_{0.2}\text{MnO}_3$

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Abstract. Lanthanum compounds of $(\text{La}_{1-x}\text{Ag}_x)_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ have been prepared for $x = 0$ and $x = 0.5$ by using sol-gel method. Bulk samples were sintered by varying temperature and duration of sintering processes. The sintering temperature was varied at two conditions, 600 °C for 5 h and 900 °C for 24 h. Crystal structure of the samples was observed by X-Ray diffraction spectrometer. Rietveld refinement of X-Ray diffraction results showed that the sample with $x = 0$, both sintered at 600 °C for 5 h and at 900 °C for 24 h are single phase and they have an orthorhombic structure with Pnma space group. The sample with $x = 0.5$ sintered at 900 °C for 24 h did not show a single phase due to the appearance of Ag peaks, and they have a perovskite structure. Meanwhile, the sample with $x = 0.5$ sintered at 600 °C for 5 h, also did not show a single phase due to the appearance of Ag and LaO peaks. This results showed that for $x = 0.5$, temperature and duration of sintering are influenced by nucleation processes in the samples. The higher temperature and more longer duration of sintering will make the nucleation processes in the sample better.

Keywords. Ag-doped, $(\text{La}_{1-x}\text{Ag}_x)_{0.8}\text{Ca}_{0.2}\text{MnO}_3$, sol-gel, and sintering.

1. Introduction

Recently, synthesis of materials with multifunctional properties is a field of intense activity, especially regarding technological innovation and development of new materials [1]. The parental material is LaMnO_3 , the fascinating materials in condensed-matter research. LaMnO_3 is an antiferromagnetic (AFM) insulator with the Neel temperature (T_N) of ~ 140 K. In order to form $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (La = trivalent rare earth element and A = alkaline earth) compounds, substituting the La site by an alkaline earth or alkaline element (A) exhibits unusual physical effects on their ferromagnetic (FM)–paramagnetic (PM) phase-transition temperature (T_C), colossal magnetoresistance and magnetocaloric effects (MCEs) [2–4].

Substitution an alkaline earth metal Ca^{2+} ion to La^{3+} ion can change the ratio of Mn^{3+} ion and Mn^{4+} ion to form perovskite $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ (LCMO). The application of LCMO is in the fields of magnetic memory devices, refrigeration, sensor, biology, medicine, and catalyst [5]. Substitution the monovalent metal Ag^+ ion to La^{3+} ion can also change the ratio of Mn^{3+} ion and Mn^{4+} ion to form $\text{La}_{1-x}\text{Ag}_x\text{MnO}_3$ (LAMO). The ionic radii of La^{3+} and Ag^+ ions are 1.18 Å and 1.13 Å, respectively. By using the ionic radii and based on a calculation of the tolerance factor, it reveals that LAMO forms a stable



manganite [6]. Physical properties of LCMO may be modified by the chemical composition as well as by various temperature and duration of sintering that is affecting to their microstructure [7, 8].

Modifying LCMO and LAMO can be done by substitution of the Ag^+ ion for La^{3+} ion to become $(\text{La}_{1-x}\text{Ag}_x)_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ (LACMO). LACMO was synthesized by a sol-gel process. Doping Ag in La site of LCMO induced an increase of Magnetoresistance (MR), Curie temperature and metal-insulator transition temperature. Furthermore, the interesting experiments have been continued by varying the synthesis process. In order to get more information in the structure, magnetic and electrical properties of LACMO, the variation of temperature and duration of sintering in the synthesis process were done. It suggests that the variation of temperature and duration of sintering in the synthesis process will influence phase and crystal structure of the sample.

2. Materials and methods

The materials of $(\text{La}_{1-x}\text{Ag}_x)_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ have been prepared by sol-gel method for $x = 0$ and $x = 0.5$. Precursors were used including of La_2O_3 , AgNO_3 , $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Each precursor was dissolved with nitric acid to obtain a transparent solution. Citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) is used with a mole ratio of citric acid of 1:1.2 from the total of metal ions. The ammonia solution is added to adjust the pH of the solution to be 7. The resulting mixture is homogenized by using magnetic stirrer at a temperature of (80 to 90) °C to form a gel. The resulting gel was heated at a temperature of 120 °C in the oven for 3 h in order to dry the sample to become high viscosity gel. After that the gel was heated at 500 °C for 5 h in the furnace to get a decomposition of the organic precursor. Then the gel was sintered with two combinations treatments at 600 °C for 5 h and 900 °C for 24 h. The obtained samples then to be characterized by using X-ray Diffraction (XRD) spectrometer and to be done for refining process to get the phase and structural analysis of the samples.

3. Results and discussion

The data of XRD of $(\text{La}_{1-x}\text{Ag}_x)_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ for $x = 0$ and $x = 0.5$ showed the characteristic peaks of the compound as can be seen in Figure 1 to Figure 4. Data of XRD signals were refined by using Rietveld method. The system was presented perovskite parameters, and unit cell volume of the LCMO and LACMO samples obtained from XRD patterns are presented in Table 1 and Table 2.

In Figure 1, the sample with $x = 0$ both sintered at 600 °C for 5 h and at 900 °C for 24 h were in single phases. They showed an orthorhombic structure with $Pnma$ space group. No change in orthorhombic structure by changing the sintered temperature from 600 °C to 900 °C and changing the duration of sintering from 5 h to 24 h but the peaks become sharper and clearer. Previous research material of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, reported by Siwach *et al*, that are sintered at 600 °C and 900 °C for 2 h and 6 h also showed the same properties of an orthorhombic structure [9].

Figure 2 showed the characteristic peaks for LACMO with $x = 0.5$. The samples did not show single phase system. It showed the appearance of another peak beside the same peaks as for $x = 0$. We found the discrepancies characteristic between two different sintering temperatures. For sintering temperature at 600 °C, we observed the appearance peaks from Ag and LaO. Meanwhile, we observed only the appearance peak from Ag for sintering temperature at 900 °C. It means that the higher sintering temperature can increase the nucleation process in the samples so the LaO peaks could be disappeared due to the melting temperature of LaO is around 900 °C. The Ag peaks were observed at $2\theta = (38.0^\circ, 44.5^\circ, \text{ and } 64.5^\circ)$ that are the same positions that are found by Irmak *et al*. in $\text{La}_{0.95}\text{Ag}_{0.05}\text{MnO}_3$ and $\text{La}_{0.75}\text{Ag}_{0.25}\text{MnO}_3$ [10]. Besides, for the Ag peaks, they still appeared due to the breaking solubility limitation of Ag^+ ions from the stoichiometric value [3]. In previous research perform by Huang and Srivastava, It has been explained that the solubility limit of Ag^+ ions should be related to $x = 0.15$. It means, in order to get single phase system, Ag concentration should be below $x = 0.15$ [11, 12]. We also observed in our previous reports [ISCPFM Nov 2017] that the single phase system could be achieved for $x < 1.5$.

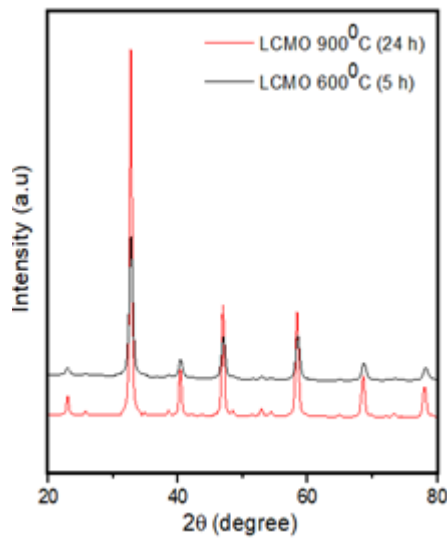


Figure 1. LCMO is sintered at 600°C (5 h) and 900°C (24 h)

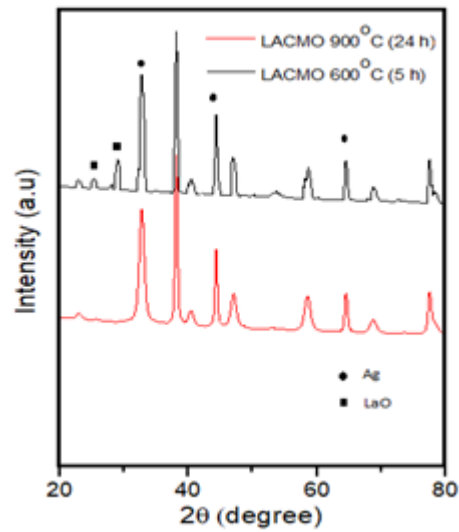


Figure 2. LACMO is sintered at 600°C (5 h) and 900°C (24 h)

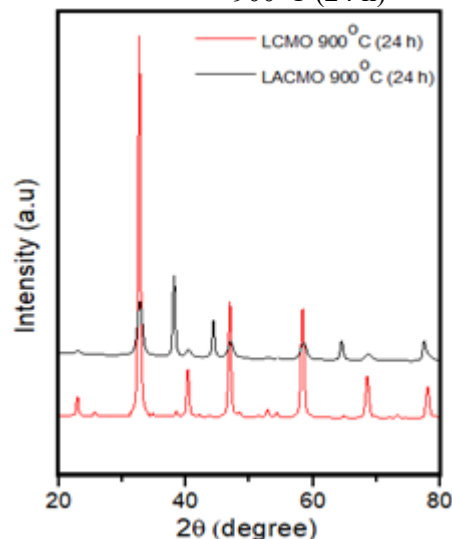


Figure 3. LCMO and LACMO were sintered at 900°C (24 h)

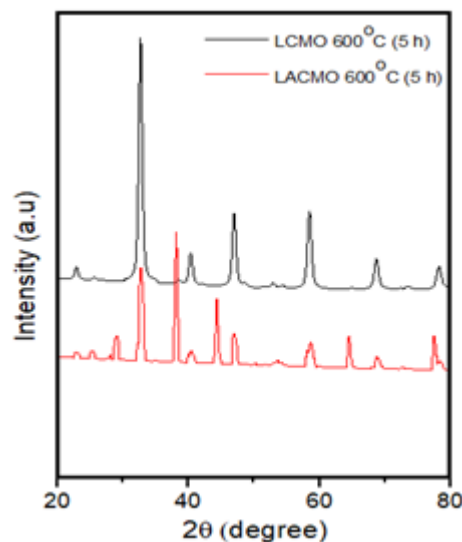


Figure 4 LCMO and LACMO were sintered at 600°C (5 h)

Figure 3 showed the differences characteristic peaks at same sintering temperature 900 °C during 24 h for LCMO and LACMO as also mentioned in Figure 4 at same sintering temperature 600 °C during 5 h. The differences are due to the appearance another phase at LACMO. The lower sintering temperature causes the appearance of more phases.

We also found that the crystallite size for $x = 0$ is 14.92 nm (sintered at 600 °C for 5 h), 25.51 nm (sintered at 900 °C for 24 h) and for $x = 0.5$ are 10 nm (sintered at 600 °C for 5 h) and 10.4 nm (sintered at 900 °C for 24 h). Crystallite size is increased with the increasing temperature and duration of sintering. We got that R profile and weighted R profile on data processing were below 10%. It means that the result is in accordance with experimental analysis which is supported by the chi-squared value of under 1.3.

Table 1. Lattice parameters, unit cell volume and goodness of fit (χ^2) LCMO and LACMO sintered at 900 °C for 24 h

Parameters	La _{0.8} Ca _{0.2} MnO ₃	La _{0.7} Ag ₁ Ca _{0.2} MnO ₃	
	Perovskite	Perovskite	Silver
a (Å)	5.4653	5.4730	4.0770
b (Å)	7.73329	7.7310	4.0770
c (Å)	5.49248	5.4880	4.0770
Volume (Å ³)	232.1383	230.3828	68.1195
Percentage of each phase (%)	100	74	26
Rp	7.3894	7.4666	
Rwp	9.3343	9.4006	
Goodness of fit	1.09674	1.1935	

Table 2. Lattice parameters, unit cell volume and goodness of fit (χ^2) LCMO and LACMO sintered at 600 °C for 5 h

Parameters	La _{0.8} Ca _{0.2} MnO ₃	La _{0.7} Ag ₁ Ca _{0.2} MnO ₃		
	Perovskite	Perovskite	Silver	Lanthanum Oxide
a (Å)	5.4638	5.4302	4.0845	4.0650
b (Å)	7.7257	7.7016	4.0845	4.0650
c (Å)	5.4595	5.5475	4.0845	6.2645
Volume (Å ³)	230.4548	232.0018	68.1415	89.6467
Percentage of each phase (%)	100	68.2	18.4	13.4
Rp	7.5812	7.6416		
Rwp	9.5221	9.5795		
Goodness of fit	1.1528	1.2399		

4. Conclusions

(La_{1-x}Ag_x)_{0.8}Ca_{0.2}MnO₃ were successfully synthesized by sol-gel process and were varied by temperature and duration of sintering with x = 0 and x = 0.5. Sintering temperature variations were done at 600 °C for 5 h and 900 °C for 24 h. For LCMO, the samples showed a single phase condition at both sintering temperature. For LACMO, the samples did not show a single phase condition due to the appearance another LaO and Ag peaks. The sintering temperature influence to the characteristic of XRD peaks. At higher sintering temperature, the peaks for both LCMO and LACMO become clearer and sharper. At LACMO the higher temperature and longer sintering duration, the samples showed decreasing numbers of the appearance phases.

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