

# Synthesis of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ( $x = 0$ and $0.2$ ) through ultrasonic mixing and its characterisation

Mangasi A M<sup>1</sup>, Iwan Sugihartono<sup>1</sup>, Teguh B P<sup>1</sup>, Sitti Ahmiatri Saptari<sup>2</sup>, and Erfan Handoko<sup>1,\*</sup>

<sup>1</sup>Universitas Negeri Jakarta, Dept. of Physics, Jalan Rawamangun Muka 13220, Jakarta, Indonesia

<sup>2</sup>Universitas Islam Negeri Syarif Hidayatullah, Dept. of Physics, Jakarta, Indonesia

**Abstract.** In order to investigate the crystal structure and morphology of perovskite manganite materials, we have been successfully synthesized  $\text{LaMnO}_3$  and  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  systems through ultrasonic mixing method. The application of these materials is the alternative cooler technology beside freon gas using with residual emission gas. Stoichiometric mixture of  $\text{La}_2\text{O}_3$ ,  $\text{MnCO}_3$ , and  $\text{CaO}$  with more than 95 % purity were prepared by ultrasonic mixing 40 kHz 60 watts for 30 minutes to result homogen mixtures. The samples were calcinated at 800°C for 1 h and sintered at 1100°C for 3 h. The structure of the samples was examined by X-ray diffractometer (XRD) Phillips and result as single phase of perovskite manganite materials. Morphology was studied using a 5310LV Jeol scanning electron microscope (SEM) that show the same grains of perovskite manganite material. While Ca substituted for La in the sample, the grain size decreases with decreasing the volume of cell units and finally the particle size of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  phase decreases.

## 1 Introduction

Freon cooling systems have been used by the public at large. The cooling system produces CFC gas that can damage Earth's ozone [1-3]. From 1881 to the last few years, research on *magnetocaloric effect* (MCE) as an alternative technology of freon cooling system [4-9] has been conducted. Broadly speaking, MCE material research is divided into two composite materials namely metal compounds and oxide compounds. In metal compounds there are three metals that have good MCE value of Gadolinium (Gd), Terbium (Tb), and Dysprosium (Dy) [1]. While the better-known oxide compound perovskite manganite material is a material composition which recently studied that due to have a better value MCE and easily synthesized from the constituent material. This material has the formula of  $\text{La}_x\text{M}_{1-x}\text{MnO}_3$  compound with  $M = \text{Li}, \text{Na}, \text{K}, \text{Ca}, \text{Sr}, \text{Ba},$  and  $\text{Y}$ . From several studies which have been done, there is an entropy change of 1.85 J / KgK on variation  $\text{La}_x\text{M}_{1-x}\text{MnO}_3$  with  $T_c = 298 \text{ K}$  [8]. Another case with the material variation  $(\text{La}_{1-x}\text{Nd}_x)_{0.75}\text{F}_{0.3}\text{MnO}_3$  becomes a commended material candidate as a cooling material with  $\Delta S = 5 \text{ J} / = 293 \text{ K}$  [1,10,11]. However, a high sintering temperature of about 1250°C and a mechanical mixing process is necessary as a condition of solid state reaction to form a manganite perovskite ceramic material. In this paper, the synthesis system  $\text{LaMnO}_3$  and  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  using *ultrasonic mixing* method with 1100 °C sintering temperature. The single phase of manganite perovskite material formed and improved microstructure are expected to achieve better results with mechanical mixing methods [2,3,10,12] and can be MCE material candidates.

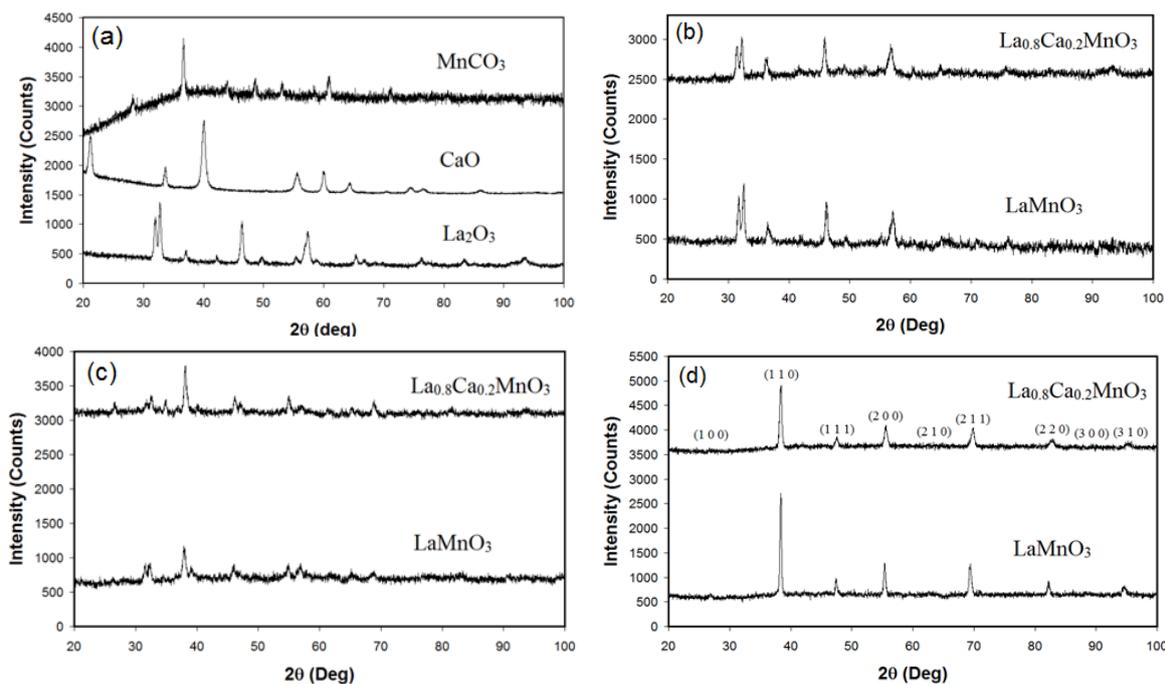
## 2 Experimental procedure

The perovskite manganite materials of  $\text{LaMnO}_3$  and  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  systems were prepared by ultrasonic mixing method. The mixing process of composite materials ( $\text{La}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MnCO}_3$ ) with a proportional amount according to their composition stoichiometry in an ultrasonic wave temperature of 40 kHz at 60 watts of power for 30 min after which it is calcined at a temperature of 800 °C for 1 hour. For the formation of the phase on the mixture was sintered 1100 °C for 3 hours after compaction at a pressure of 5 tons diameter of 20 mm. The orthorhombic crystal structured material is measured by Phillips x-ray diffraction  $\text{Co-K}\alpha$  at angle interval ( $2\theta$ ) 20° - 100° data processing with High Score Plus Version 3.0e PANalytical software. Observation of morphology of phase grains using scanning electron microscope (SEM) 5310LV Jeol.

## 3 Results and discussion

The x-ray diffraction pattern of all material constituents in this study is shown in Figure 1a. The identification results provide information that the constituents used have a purity level of more than 95% and impurities less than 4% do not appear diffraction peaks. Figure 1b is an x-ray diffraction pattern after optimally mixing through the ultrasonic process for both compositions. The same peak pattern shape ensures a homogeneous mixture. Whereas in Fig. 1c is the result after the calcination process at temperature of 800 °C for 1 hour and shows that all compositions have occurred atomic diffusion which is the formation of manganite perovskite phase.

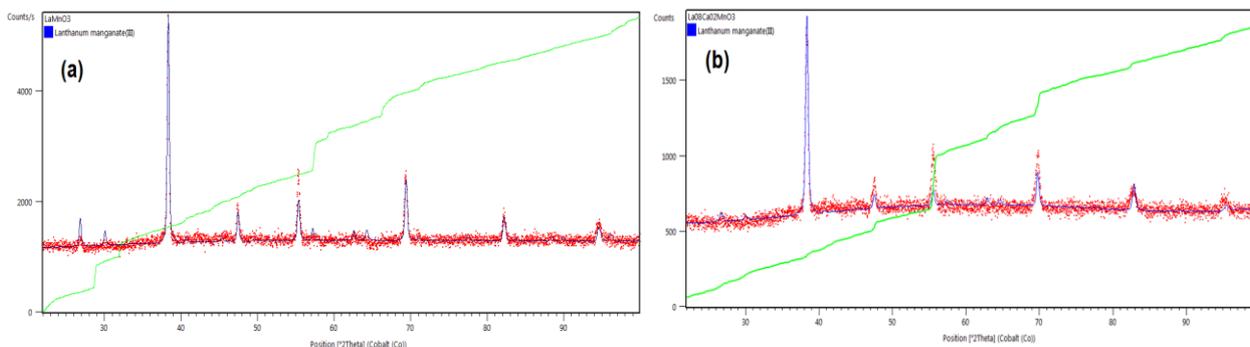
\* Corresponding author: [mangasi@unj.ac.id](mailto:mangasi@unj.ac.id); [erfan@unj.ac.id](mailto:erfan@unj.ac.id)



**Fig. 1.** X-ray diffraction pattern: (a) constituent material, (b) ultrasonic mixing process, (c) calcination process, and (d) after sintering process.

The 1100 °C sintering process for 3 hours against both compositions of 20 mm diameter solids ensures that LaMnO<sub>3</sub> and La<sub>0.8</sub>Ca<sub>0.2</sub>MnO<sub>3</sub> systems are formed as expected (Figure 1d). The result of qualitative analysis of diffraction pattern in Fig. 1d shows that manganite perovskite phase has been formed for both compositions.

However, there has been a high-intensity difference and there has been a shift to the peak point around the(2θ) 38.44° angle and this also show that there has been Ca substitution seen from both compositions.

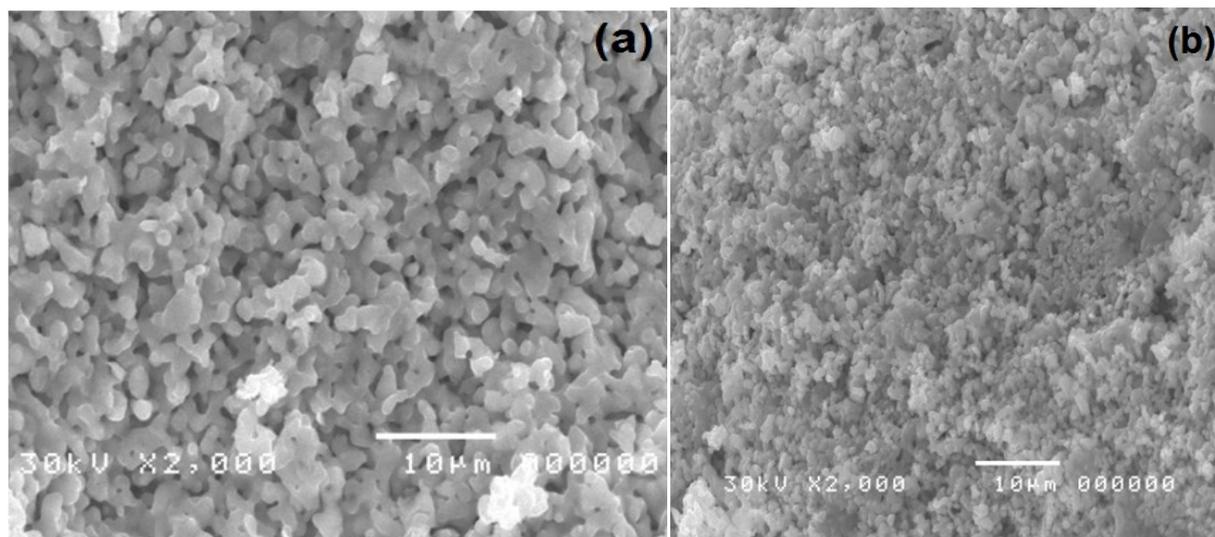


**Fig. 2.** Refinement results of x-ray diffraction pattern data after sintering processfor (a) LaMnO<sub>3</sub> and (b) La<sub>0.8</sub>Ca<sub>0.2</sub>MnO<sub>3</sub>.

The results of quantitative analysis of light diffraction data by refinement process (Fig. 2) using the software of HighScore Plus Version 3.0e PANalytical obtained orthorhombic crystal structure with lattice constants respectively 0,545 nm (a), 0,769 nm (b), 0,544 nm (c) for LaMnO<sub>3</sub> and 0.539 nm (a), 0.763 nm (b), 0.538 nm (c) for La<sub>0.8</sub>Ca<sub>0.2</sub>MnO<sub>3</sub>. There has been a change of constant lattice change due to substitution of Ca to La which

resulted in the change of unit cell volume to decrease from 0,228 nm<sup>3</sup> to 0,222 nm<sup>3</sup>.

The morphological observations of the microstructure with SEM at 2000 magnification shows the form of particles, which are particles of many crystals (polycrystalline) of different sizes for both compositions.



**Fig. 3.** SEM photographs the microstructure morphology of perovskite materials of the system (a)  $\text{LaMnO}_3$  and (b)  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ .

The particle size on a micrometer scale is uniformly homogenous for  $\text{LaMnO}_3$ . However, the effect of Ca substitution on La resulted in smaller particle size compared to  $\text{LaMnO}_3$  particle size. This can be ascertained as a result of the smaller unit cell volume. In addition supported by the calculation of crystallite size with Scherrer method obtained the average size for 39.4 nm for  $\text{LaMnO}_3$  and 28.8 nm for  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ .

#### 4 Conclusions

In conclusion, the perovskite material of  $\text{LaMnO}_3$  and  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  systems prepared by ultrasonic mixing method has been successfully manufactured and is a polycrystalline material. The focus of the research in the analysis of crystal structure and morphology of microstructure resulted from the formation of single phase manganite perovskite material and the process of substitution of Ca to La resulted in the change of lattice constants which decrease with the initial cell unit volume of  $0,228 \text{ nm}^3$  to  $0,222 \text{ nm}^3$  and also followed by decreasing the crystal size. The decrease in unit cell volume results in a decrease in the size of the grain (cereal grain) after substitution and also based on the morphological observation of the microstructure with SEM the particle size diminishes.

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