

EFFECT OF SUBSTITUTION OF Al³⁺ into La_{0.67}Sr_{0.33}MnO₃ SYSTEM USING SOL-GEL METHOD

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ABSTRACT

Thin film samples of La_{0.67}Sr_{0.33}Mn_{1-x}Al_xO₃ were synthesized using sol-gel method with $x = 0.00, 0.15$ and 0.30 . Nitric acid, triethanolamine (TEA) and distilled water were used as solvent and stabilizer agent. All the samples were calcined at 650°C and 750°C for half an hour. The structural morphology was investigated via x-ray diffraction (XRD) and scanning electron microscope (SEM). X-ray diffraction patterns show rhombohedral distorted perovskite structures. The scanning electron microscope showed the average grain size was decreased as the level of doping concentration increased and structural orientation is more ordered. Magnetic properties were investigated using vibration sample Magnetometer (VSM) at room temperature. Analysing all the samples show when magnetic field is getting higher, magnetization of the samples decreased.

Keywords: Sol-gel method; rhombodehral; perovskite structures; magnetization;

INTRODUCTION

Alkaline earth-substituted lanthanum manganates (La_{1-x}A_xMnO₃, A = Ca, Sr and Ba) have perovskite type structure, that can show fine electric conductivity, catalytic, mechanical and colossal magnetoresistance (CMR) properties, which have attracted a lot of attention [1-3]. Thin films of manganese oxides Re_{1-x}A_xMnO₃ where Re is a rare earth (La) and A is alkali earth element such as Ca, Sr, Ba [4]. Microstructure of the film usually drastically alters the temperature and low-field behaviors of MR, and so play an importnat role in the magnetotransport properties. Among the factors that can influence the microstructure, the preparation route, substrate and annealing temperature are emphatically considered [5]. Objective for this work is to investigate the effect of substitution Al₂O₃ into La_{0.67}Sr_{0.33}MnO₃ system on the structural morphology and

magnetic properties of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ samples with $x = 0.00, 0.05$ and 0.10 where samples was calcined at different temperature.

METHOD

Experimental was setup to synthesis $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ using sol-gel method. $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$ and Al_2O_3 were dissolved in nitric acid, triethanolamine (TEA) and distilled water. Triethanolamine was used to prevent the colloidal particles of chelate from aggregation. The molar ratio of metal ion and nitric acid was 1:2. The final solution was filtered and spin coated on ITO glass and quartz. ITO glass and quartz substrate was used with dimension (10mm x 10mm) was cleaned with acetone and methanol. After that, substrates was rinsed with deionized water and dried. Samples were spin coated on the substrate with rpm 3850 rev/min with 3 repeated layers. Samples were heated at 90°C to remove water from the samples. Samples was calcined at 650°C and 750°C with heating rates at $1^\circ\text{C}/\text{min}$ and cooling rate at $1^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSIONS

Scanning electron microscope (SEM) measurement was used to investigate the microstructure of $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ with different concentration of x which shows different size distribution of particles. Samples $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for $x = 0.00, 0.05$ and 0.10 without dopant Al shows different structures. Microstructures of the samples did not show any clear particle that can be seen. For these samples, the particle that produced showed rod structures when the concentration of x increased and surface structures look likes more brittle as the concentration of x increased. Samples for $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ where $x = 0.05$ and 0.10 show different kind of structure. It clearly can be seen the particles size where the average particle size of undoped and doped of Al compound are slightly different. Calcinations of doped Al_2O_3 into $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ system enhance the particle to form more clear and compact particles. As the concentration of x increased, the size particles decreased but the structural become more compact.

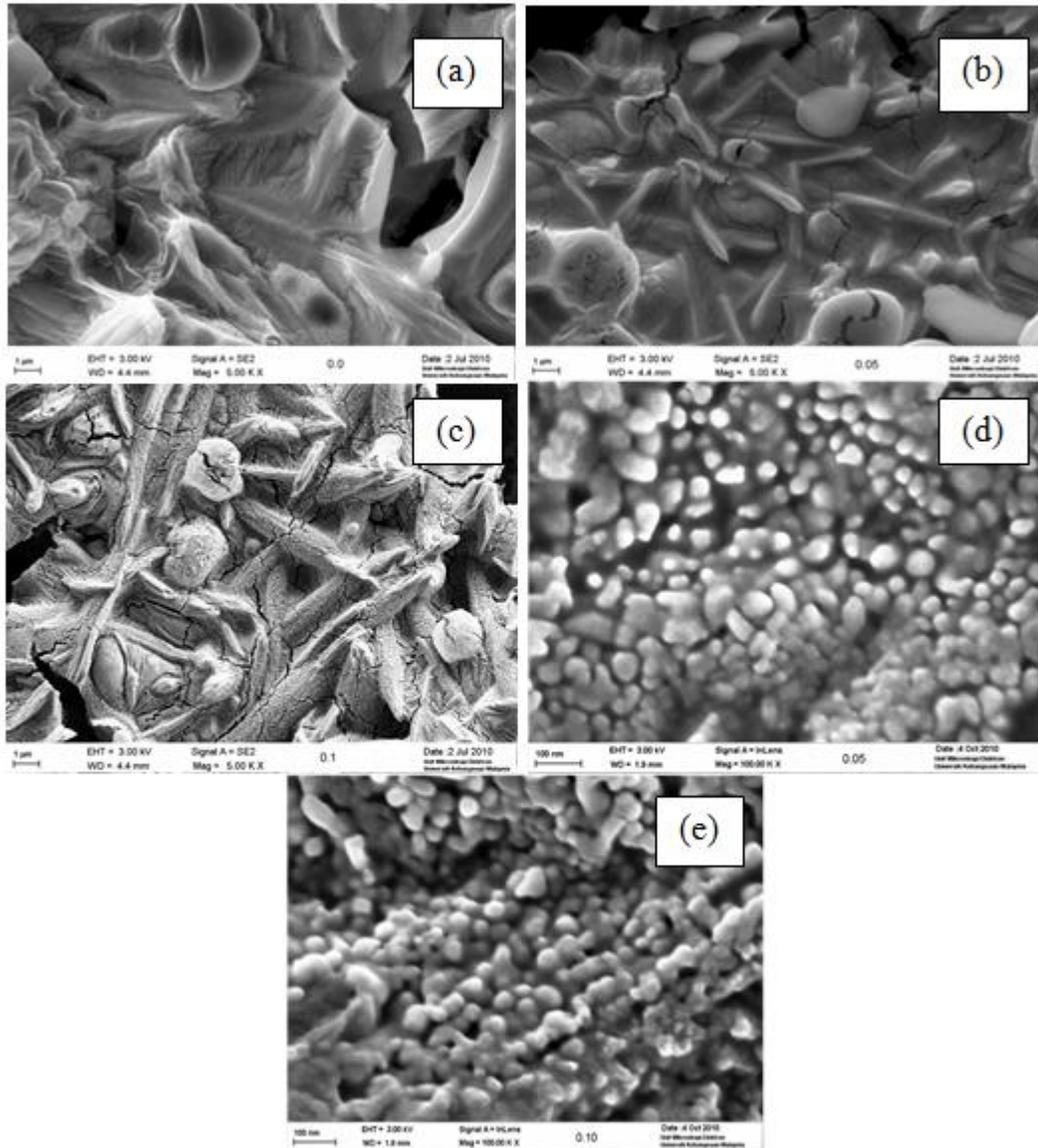


Figure 1: Scanning electron microscope (SEM) of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ undoped, (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ doped with Al_2O_3 , (c) $x = 0.05$, (d) $x = 0.10$

X-ray diffraction patterns are shown in Figure 2 as deposited thin film with different dopant concentration. The XRD pattern show the single phase with rhombohedral distorted perovskite structures. Indices miller (104) direction has been observed as dominant peak between 25° and 35° . This indicates that for samples LSMO had fine crystal structures compared with other samples. According to Li [6], the orbital degeneracy leads to a Jahn-teller instability, which caused the oxygen octahedral to distorted and lower its site symmetry to orthorhombic and thus remove an orbital degeneracy.

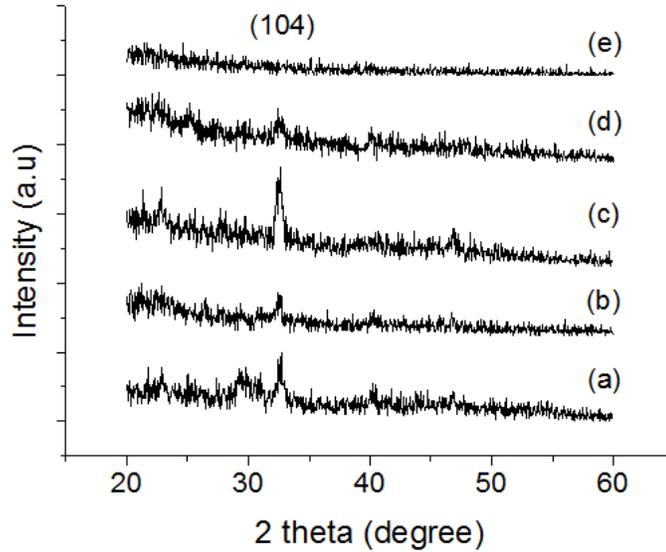


Figure 2: X-ray diffraction (XRD) graph pattern of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ undoped, (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ doped with Al_2O_3 , (c) $x = 0.05$, (d) $x = 0.10$

The magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ thin film was investigated at room temperature by using the vibration sample magnetometer (VSM). Figure 3 shows the VSM graph pattern for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ sample with the concentration of $x = 0.00, 0.05$ and 0.10 and for doped $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ sample with concentration of $x = 0.05$ and 0.10 . The graph pattern that was obtained is known as magnetization curve or hysteresis loop and also the pattern of a hysteresis graph were influenced by the concentration of x . Based on Figure 3, the graph pattern show that for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples for $x = 0.15$ shows the highest value of magnetization which is $4.78 \text{ M}(\text{emu/g})$ compared with other samples. Magnetization value for $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ samples for $x = 0.00$ and 0.05 are $0.06 \text{ M}(\text{emu/g})$ and $0.081 \text{ M}(\text{emu/g})$. The graph pattern for $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ samples for $x = 0.05$ is $0.1855 \text{ M}(\text{emu/g})$ and for $x = 0.10$ is $0.0287 \text{ M}(\text{emu/g})$. This can be explained by the transportation electron within single magnetic domain. The e_g electrons transfer between $\text{Mn}^{3+}/\text{Mn}^{4+}$ ions is easy and lead to decrease in MR. The pairs of Mn^{3+} and Mn^{4+} spin which not be parallel in the vicinity of domain wall boundaries, act as obstacle for electron transport [7].

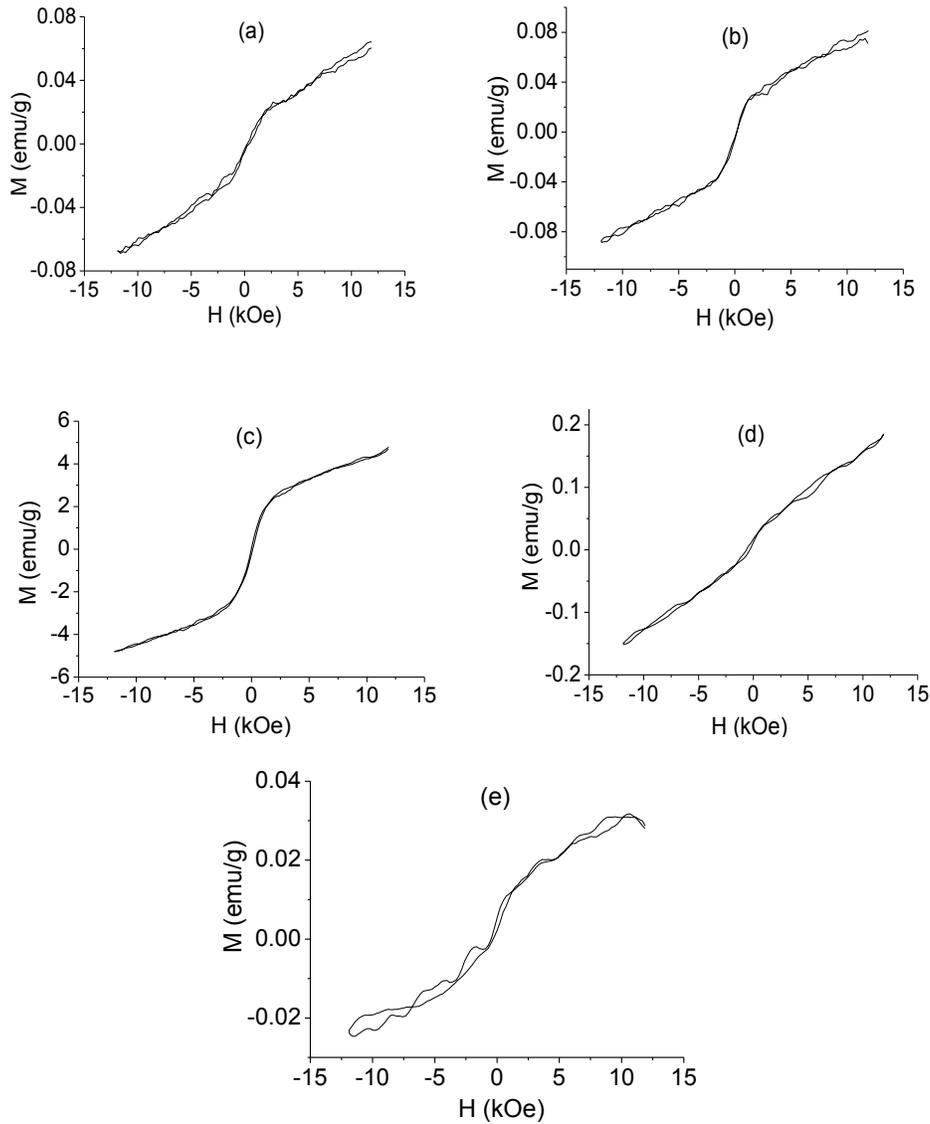


Figure 3: Vibration sample magnetometer (VSM) pattern of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ undoped, (a) $x = 0.00$, (b) $x = 0.05$, (c) $x = 0.10$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ doped with Al_2O_3 , (c) $x = 0.05$, (d) $x = 0.10$ at room temperature

CONCLUSION

Samples of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.00, 0.05$ and 0.10) $\text{La}_{0.67}\text{Sr}_{0.33}\text{Mn}_{1-x}\text{Al}_x\text{O}_3$ ($x = 0.05$ and 0.10) thin films were successfully synthesized by sol gel method at room temperature. All the samples were deposited on quartz substrate using spin coated technique. From SEM microstructures, it shows that the different morphology has been obtained after Al_2O_3 compound has been introduced into LSMO system as the concentration of dopant increased. XRD pattern showed that a single phase with rhombohedral distorted

perovskite structures. Magnetic properties has been obtained at room temperature where the highest magnezation value has been obtained with sample $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ for $x = 0.10$.

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