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Structural and Magnetic Studies of Undoped and Strontium-Doped Lanthanum Manganite System

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ABSTRACT

Lanthanum strontium manganite perovskites are the most studied cathode materials for solid oxide fuel cells. Lanthanum manganite and strontium doped lanthanum manganite belong to the perovskite oxide family. The larger rare earth ion (e.g., La) occupies the 12 coordinated A-sites and the transition metal ions (e.g., Mn) occupy the octahedral B sites. Both the electrical conductivity and catalytic activity of lanthanum manganite are enhanced considerably when lanthanum is substituted partially with strontium. In this work, the effect of Sr doping on the composition, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0, 0.1, 0.3, 0.5$) has been studied. The perovskite oxides have been synthesized by the conventional ceramic route. The synthesized powders were characterized by X-ray diffraction, scanning electron microscopy. The magnetic studies were done by an alternating gradient magnetometer. The XRD patterns of all the samples clearly shows the formation of crystalline perovskite structure, however the LSM samples with $x=0$ and 0.1 shows a small amount of La_2O_3 . The magnetic measurements of the samples were realized at room temperature and all samples displayed superparamagnetic properties with coercive fields near to zero. This behavior is originated from the surface spin disorder enhancement caused by decreasing particle size.

Keywords: Perovskite, cathode, lanthanum strontium manganite



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1. Introduction

Solid oxide fuel cells (SOFCs) are the most efficient and environmentally friendly energy conversion technology to generate electricity from fuels as compared to the conventional thermal power generation plants [1]. However, there are many material problems to be solved due to the high temperature operation ($\sim 1000^{\circ}\text{C}$) of the SOFC system. The main factor limiting the performance of SOFC is the significant material limitations imposed by the cathode and the cathode leads because of the high corrosion effect of oxygen at high operating temperature. The cathode material has to meet some requirements like high electronic conductivity, thermal and chemical stability, and good compatibility with the solid electrolyte, sufficient porosity for the oxide ions to migrate, and good adherence at the surface of the electrolyte to work at high operating temperature in air or oxygen atmosphere. Some complex oxides in the perovskite family may satisfy the above mentioned requirements and has been widely studied in recent years for use as cathode materials for SOFCs [2].

Perovskite type oxides of the ABO_3 structure with trivalent rare earth in the A position and trivalent transition metal ions in the B position are p-type conductors. Lanthanum manganite ($\text{LaMnO}_{3\pm\delta}$) belongs to perovskite oxide family and can crystallize either with orthorhombic or rhombohedral symmetry depending on the value of δ , and it may depend on many factors like method of synthesis, thermal treatments etc. [3,4]. The larger rare earth ions (La) occupy the 12 coordinated A-sites and the transition metal ions (Mn) occupy the octahedral B-sites. The substitution of A-site cations by aliovalent cations forms oxygen vacancies and causes a change in the valence states in B-site cations so that charge neutrality can be maintained. As a result, the perovskite oxide shows substantial electronic conductivity as well as ionic conductivity at elevated temperatures. When lanthanum is substituted partially with strontium, the electrical conductivity and catalytic activity of lanthanum manganite can be considerably increased. Though lanthanum strontium manganite (LSM) as cathode material have proved to be a poor oxygen ion conductor, its electronic conductivity is high enough to make them the most investigated cathode materials for solid oxide fuel cells. With high electronic conductivity, LSM offers a high catalytic activity for oxygen reduction as well as chemical and thermal compatibility with the conventional yttria stabilized zirconia electrolyte at the operating temperature [5].

The perovskite $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ exhibits a variety of magnetic phases, the end member $x=0$ is an antiferromagnetic insulator due to the superexchange between Mn^{3+} ions. The substitution of Sr in La sites of the LaMnO_3 phase leads to a ferromagnetic double exchange interaction, metallic conductivity and a large magnetoresistance [6]. Due to the mixed valence states of manganese ions, their spin states fluctuate between trivalent and quadrivalent states. In this study, conventional ceramic route was adopted for the synthesis of perovskite oxides and the analysis of crystal structure, magnetic and electrical properties of the synthesized samples were done by different techniques. Here we



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report the effect of strontium substitution on lanthanum manganite on the crystal structure and magnetic properties of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ system, where ($x=0, 0.1, 0.3, 0.5$).

2. Experimental procedure

Powders of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0, 0.1, 0.3, 0.5$) were prepared by a high temperature solid state reaction by using the high purity (Aldrich 99.99%) oxides, La_2O_3 , $\text{Sr}(\text{NO}_3)_2$ and MnO_2 . The rare earth oxide, La_2O_3 was fired overnight at 800°C before using, in order to decompose the hydroxides, carbonates and oxycarbonates present. The stoichiometric amounts of the starting materials were milled for 2 hrs after being thoroughly mixed in methanol. The obtained material was calcined at 1000°C in air for 12 hr. Then they were ground and calcined in air at 1200°C for 12 hr and ground again to obtain fine powders.

The crystal structure of the synthesized samples were done by X-ray diffraction (XRD) in a Philips X'Pert diffractometer using Ni filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5418\text{\AA}$). The chemical analysis and morphology of the synthesized powders and sintered pellets were done by JEOL-JSM-6300 Scanning Microscope. The specific surface area (S_{BET}) values were determined by BET method (Nova 2000, Quanta-Chrome). The average particle size (D_{BET}) was calculated assuming the presence of spherical particles, by means of the equation

$$D_{\text{BET}} = \frac{6}{S_{\text{BET}} \rho}$$

where ρ is the theoretical density of LSM (6.45 g/cm^3). The magnetic properties were measured at room temperature in an alternating gradient magnetometer (AGM Micromag 2900) manufactured by Princeton Measurement Corporation.

3. Results and Discussions

The X-ray diffraction patterns of $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$ (where $x=0, 0.1, 0.3$ and 0.5) samples prepared by solid state reaction are shown in Fig.1. The XRD patterns of all the samples clearly shows the formation of crystalline perovskite structure, however the LSM samples with $x=0$ and 0.1 shows a small amount of La_2O_3 along with the rhombohedral phase. It is reported that in solid state reaction experiments, the presence of perovskite type phase in the first reaction step, but some of the La_2O_3 does not react and it takes very long firing times at high temperatures to have the La_2O_3 reacted completely with four or five intermediate grindings [7]. In our case, LaMnO_3 shows a rhombohedral phase and with the substitution of 10 and 30 mole% of Sr to LaMnO_3 , the perovskite structure still shows a rhombohedral symmetry. When the strontium content increases upto to 50mole%, the perovskite structure adopts an orthorhombic symmetry. A slight shift of all peaks was observed in the direction of increasing diffraction



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angles as the strontium doping level increased from $x=0.1$ to 0.5 , and there is a significant broadening of the peak with increasing Sr content.

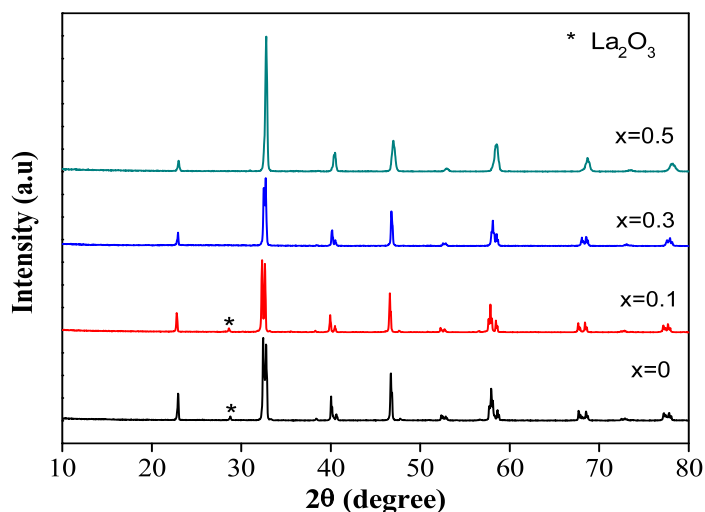


Figure 1. XRD patterns of the synthesized samples $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$, where $x=0, 0.1, 0.3$ and 0.5

When La^{3+} is doped with lower valence cations like Sr^{2+} , leads to increase electronic disorder and changes in the oxidation state of the 3d transition metal and in the oxygen non-stoichiometry, which increases the concentration of Mn^{4+} in LaMnO_3 , since the ionic radii of Sr^{2+} (1.44 \AA) is slightly larger than La^{3+} (1.36 \AA) respectively. The crystallite size of all the samples were calculated by using the Scherrer equation by considering (204) peak at $2\theta = 46.7^\circ$ for the rhombohedral phase and (112) peak at 32.7° for the orthorhombic phase [8]. The crystallite sizes of all samples were found to be in the nanosize range and are shown in the Table 1.

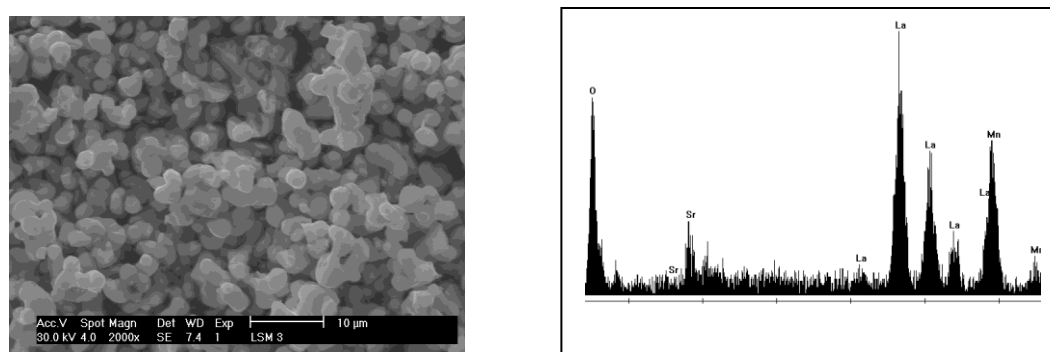


Figure 2. SEM micrographs and EDAX analysis of the synthesized sample with $x=0.1$

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The morphology of the particles in ceramic materials is the consequence of the preparation method. Figure 2 shows the SEM and EDAX analysis of the LSM powders; it shows the formation of agglomerates of fine primary particles with porous structure. Table shows the values of crystallite size, surface area, pore volume, average particle size and pore size of the LSM powders synthesized by solid state method. Crystallite size is found to decrease with increase in Sr amount and an increase in specific surface area.

Table1. Average crystallite size (D_{XRD}), specific surface area (S_{BET}), pore volume (V_{pore}), average crystallite size (D_{BET}) and pore size of the sample powders

Composition	Crystallite size (nm)	Surface area (S_{BET})(m ² /g)	Pore volume cc/g	Average particle size (D_{BET}) (μm)	Pore size (Å°)
x=0	67.48	1.052	0.0025	0.88	31.69
x=0.1	77.87	0.601	0.0015	1.55	31.69
x=0.3	70.97	0.992	0.0034	0.94	31.69
x=0.5	59.18	2.027	0.0070	0.46	31.69

Scanning electron micrograph of the synthesized sample with x=0.5 sintered at 1500°C is shown in figure 3. The porous structure is also evident even if the sample sintered at 1500°C. With sintering the grains agglomerate and grow, the number of the open pores reduces, and the open pores are located at the multigrain boundaries.

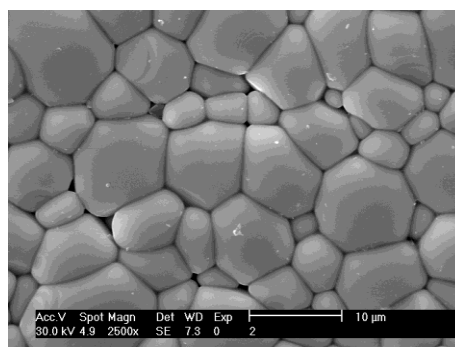


Figure 3. SEM micrographs of the sample with x=0.5 sintered at 1500°C

The magnetic properties of LSM samples are shown in figure 4. The magnetization hysteresis loop of LSM sample with x = 0.5 is displayed in figure 4(a), it can be observed that LSM samples exhibit superparamagnetic properties with both coercive field and remanent magnetization near to zero, this behavior is related with the nanostructured nature of the powders. In figure 4(b), the changes of saturation magnetization with x are shown, it is clear that Sr impurities plays an important role on the magnetic properties, although a non linear effect with concentration of x is observed. The non linear behavior can be due to the fact that the prepared powders are not pure and the quantification of additional oxide phases is hard to be determined. For future works, a more specific route for

formation of pure LSM powders have to be realized, this will help to have more realistic effect of Sr impurities on the magnetic properties of nanostructured LSM powders.

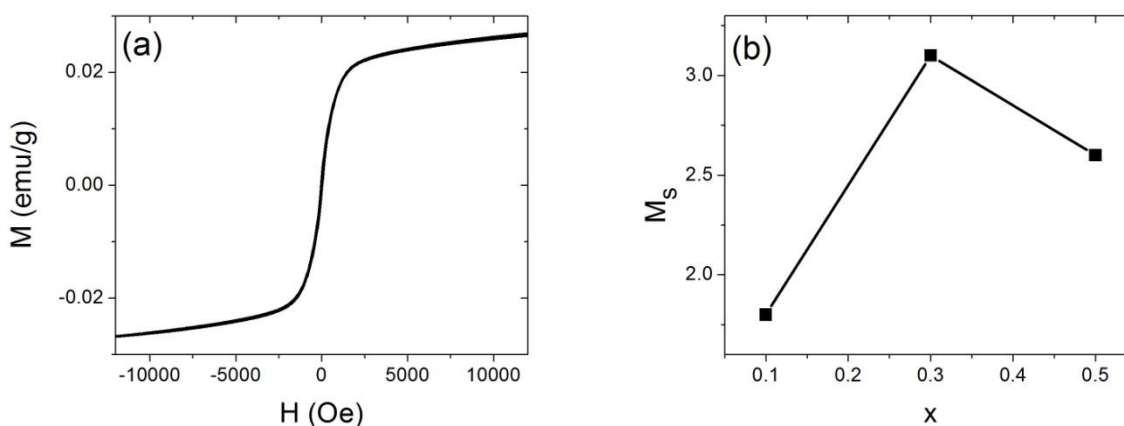


Figure 4. Magnetic properties of LSM samples. (a) Magnetization vs magnetic field for sample $x=0.5$, (b) saturation magnetization (M_s) vs x .

4. Conclusions

Perovskite structured $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x=0, 0.1, 0.3, 0.5$) powders was prepared by the conventional solid state synthesis. The nanocrystallite sizes of the powders ranged between 59-77nm. Crystallite size is found to decrease with increase in Sr amount and specific surface area increases. LSM samples exhibit superparamagnetic properties with both coercive field and remanent magnetization near to zero, which can be related to the nanostructured nature of the powders.

5. Acknowledgements

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