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# Influence of Eu doping on magnetocaloric behavior of $La_{0.67}Sr_{0.33}MnO_3$

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ABSTRACT

Colossal Magneto Resistance (CMR) materials with the compositional formula, $La_{0.67-x}Eu_xSr_{0.33}MnO_3$ (where $x = 0.3, 0.33, 0.36$ and $0.39$) were prepared by the sol–gel method. After characterizing the samples structurally, a systematic investigation of magnetization has been undertaken, over a temperature range 70–300 K under 0.05 T magnetic field. An effort has been made to calculate the magnetocaloric behavior of all the samples theoretically using the experimental magnetization data. Magnetocaloric effect parameters such as maximum entropy change, full width at half-maximum and relative cooling power under 0.05 T were computed. The observed behavior has been explained qualitatively.



## 1. Introduction

In recent times, the magnetic refrigeration based on Magneto Caloric Effect (MCE) phenomenon has attracted considerable attention of the scientific community because of its environmental friendly and energy efficient features compared with those of traditional gas compression refrigeration ones [1]. A suitable magnetic material for this purpose should possess a large magnetic entropy change ($\Delta S_{max}$), high adiabatic temperature change ($\Delta T_{ad}$), excellent Refrigerant Capacity (RC) etc., when subjected to magnetization and demagnetization process. For this purpose, a large number of investigations were carried out on variety of materials such as inter metallic compounds, metals and rare earth alloys which have high total angular momentum quantum number. Some of the compounds on which extensive work was carried out are Gd [2], $Gd_5(Si_2Ge_2)$ [3] and MnP [4]. In fact, the largest reported value of the magnetic entropy change in these materials was 13.7 J/kg K in undoped Gd at 293 K under a magnetic field change of 8 Tesla [5]. In recent past, increasing attention has been focused on large magnetocaloric effects in perovskite-type manganese oxide [6,7]. It was reported that several materials of this type have even larger magnetic entropy changes at Curie temperature than the undoped Gd. A large magnetic entropy change was found in manganites exhibiting CMR behavior [8–10], suggesting that these materials might be exploited for magnetic refrigeration applications. Moreover, additional advantage with these materials is that they are less expensive when compared with those of Gd based ones.

In view of these facts, efforts have been going on in this laboratory for the last few years to investigate the magnetocaloric behavior of some of manganites. For this purpose, a series of manganites have been chosen and investigated [11,12]. In the present investigation, Eu doped $La_{0.67}Sr_{0.33}MnO_3$ samples have been taken up and the results of such an investigation are presented in this paper. In fact, when Eu is doped the average A-site ionic radius $\langle r_A \rangle$ decreases which in turn reduces the one electron bandwidth ($W$) of $e_g$ band via variation of bond angles and bond lengths of $MnO_6$ octahedra. The variance parameter also increases with increasing Eu content, influencing magnetic as well as magnetocaloric properties [13,14].

## 2. Experimental details

Colossal magnetoresistive materials (CMR) with a compositional formula, $La_{0.67-x}Eu_xSr_{0.33}MnO_3$ (where $x = 0.3, 0.33, 0.36$ and 0.39) were prepared by the sol–gel route using metal nitrates as the starting materials. More details about the preparation of these materials are given in an earlier publication [15]. The precursor powders were calcined at 1100 °C for 8 h and finally sintered at 1350 °C for 6 h in air. The structural characterization of these samples was carried out by powder X-ray diffraction (XRD) using a Rigaku Rotaflex RTC 300 RC diffractometer with Cu$K\alpha$ radiation and the data were analyzed using the Fullprof Rietveld refinement technique. The surface morphological studies of all the materials were carried out by a scanning electron microscope (SEM, HITACHIS-4800) after sputter-coating the samples with platinum. Finally, the magnetization measurements were performed using

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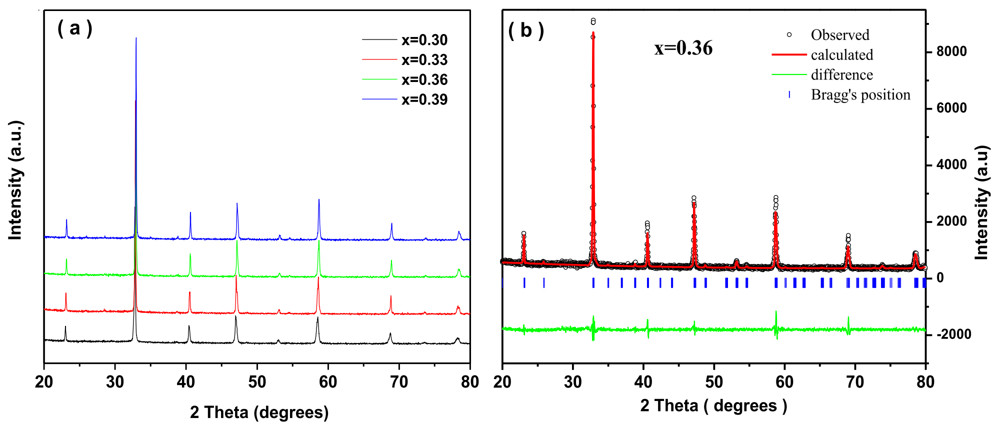


**Fig. 1.** (a) X-ray diffraction patterns of $La_{0.67-x}Eu_xSr_{0.33}MnO_3$ samples. (b) Rietveld refinement of $La_{0.31}Eu_{0.36}Sr_{0.33}MnO_3$ sample.

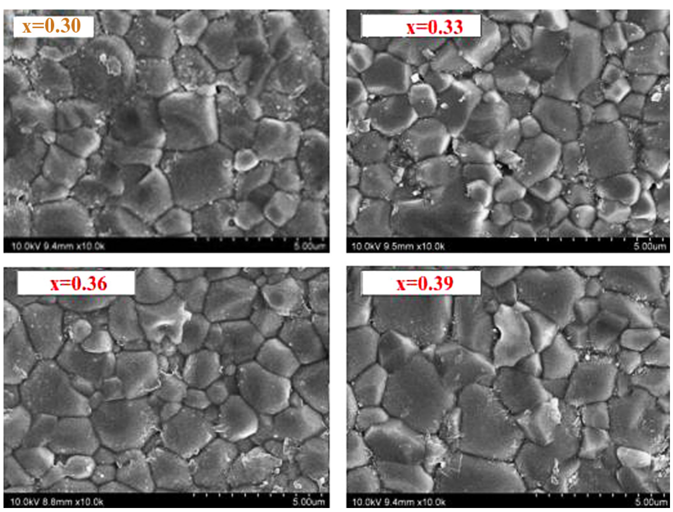


**Fig. 2.** (a–d) SEM photographs of $La_{0.67-x}Eu_xSr_{0.33}MnO_3$ samples.

a Vibrating Sample Magnetometer (VSM) (Lake Shore model No. 7460).

## 3. Results

The structural investigation of the samples was carried out by XRD studies and the powder diffraction patterns of the samples are shown in Fig. 1(a). The XRD data were analyzed using Rietveld refinement technique assuming orthorhombic structure with *Pnma* space group and more details are given in an earlier publication [15]. A typical plot of XRD pattern of $x = 0.36$ sample along with its Rietveld refined one, including the difference between the observed and calculated patterns is shown in Fig. 1(b). It is clear from the XRD data that all the samples are having single phase, without any detectable impurity.

It is known that from the SEM micrographs one may find information regarding the size and shape of grains along with the porosity, if any. The properties of the manganites are expected to be critically dependent on the grain sizes of the samples. In view of this, SEM studies were undertaken to understand the microstructure of the samples and Fig. 2(a)–(d) shows their images. The grains are clear with well-defined boundaries with large grain sizes of as large as 2–3 μm. The large grains might be due to the fact that the samples were sintered at high temperature of 1350 °C.

Manganites are known for exhibiting clear and well defined transitions, especially at their ferro to paramagnetic transition temperatures. Therefore, a systematic investigation of magnetization with temperature was undertaken and the magnetizations versus temperature plots are shown in Fig. 3(a). The open circles indicate the experimental magnetization data, while the lines indicate theoretical fittings. From the figures one may observe the magnetization of all the samples after remaining constant is found to increase suddenly and then remains constant on further decrease of temperature. The ferro to paramagnetic transition temperatures ($T_C$) were given in Table 1. The transition temperatures are found to decrease with increasing the Eu concentration. The observed behavior may be attributed to the fact that as Eu content increases, the average A-site cation radius decreases leading to the enhance-

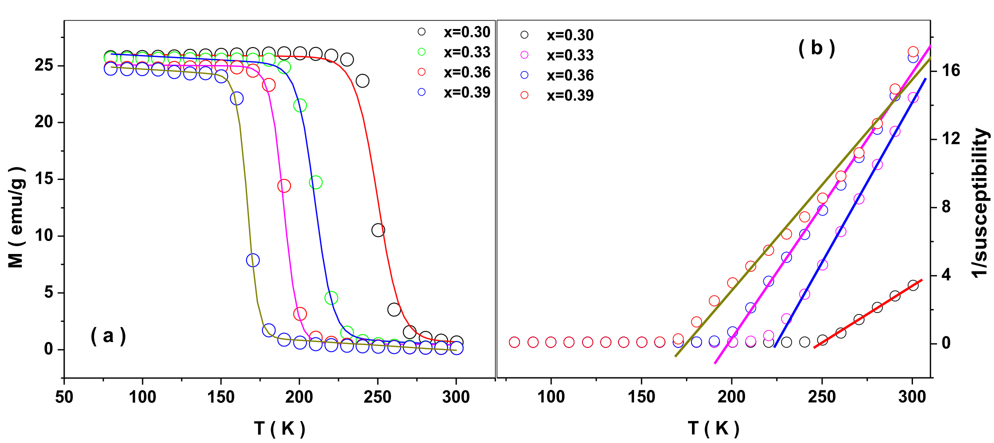


**Fig. 3.** (a) Temperature dependence of magnetization of $La_{0.67-x}Eu_xSr_{0.33}MnO_3$ system at 0.05 T applied magnetic field. Empty circles represent the experimental data and lines represent the fitting curves. (b) Curie–Weiss law fittings of $La_{0.67-x}Eu_xSr_{0.33}MnO_3$ samples.