Chapter 3

A Brief Review on Magnetic and Magnetocaloric Properties of La-Type Manganites

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Abstract

In present chapter, experimental techniques and preparation conditions adopted for the synthesis of La-type manganites and their influence on the structural, magnetic and magnetocaloric properties are briefly reviewed. The effects of various strategies of substitutions on magnetic and magnetocaloric properties are addressed. Further, our synthesis and findings on Mn-Fe substituted manganites are presented. It was found that partial substitution of Mn by Fe results in decreasing the magnetization and the Curie temperature, but the magnetic entropy change values remained in the range suitable for magnetic refrigeration.

Keywords

Synthesis of Manganites, Structural and Magnetic Properties, Magnetic entropy, RCP

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1. Introduction

Magnetic materials have acquired great scientific, as well as industrial and technological interest due to their crucial role in the fabrication of essential components for a multitude of devices and machines in active use nowadays. The search for new magnetic materials for high performance magnetic entropy for applications has led to an exponential growth in both the scientific research in this field, and the investment in the development of such materials. This development in materials research was driven by the evolution of new technologies, and the ever-increasing demand for the improvement in efficiency, better machine designs, and device miniaturization.

A great deal of work had been carried out concerning the substitution effects of Mn cations in B-sites by trivalent and tetravalent ions such as Fe, Co, Mo, and Cr [1-5]. In fact, colossal magnetoresistance (CMR) and magnetocaloric effect (MCE) in various perovskite oxide manganites has become a topic of considerable research interest due to their potential applications for devices, and the challenge to fully understand the basic nature of the strong interplay between magnetic order, electronic transport, structural distortions, and elastic properties in these materials. Generally, the CMR and MCE effects are explained by double-exchange (DE) mechanism, which considers the transfer of one eg electron between neighboring ions through the Mn$^{3+}$- O$^{2-}$- Mn$^{4+}$ path [6, 7], and the dynamic Jahn-Teller (JT) distortions caused by a strong electron–phonon coupling in manganites [8]. To better understand the metal-insulator transition, the CMR and the MCE, it is essential to understand the nature of the paramagnetic (PM)-ferromagnetic (FM) transition. Moreover, many studies on the critical behaviors as well as the universality class around the Curie temperature ($T_C$) have indicated that the critical exponents play important roles in elucidating interaction mechanisms near $T_C$ [9, 10]. The discontinuous FM-PM transition at $T_C$ is accompanied by structural changes, and is known as a first order magnetic transition (FOMT) [11-13]. This discontinuous phase transition can be rounded to a continuous one of a second order magnetic phase transition (SOMT) upon the doping, reduced dimensionality and external fields [14]. To make these
issues clear, it is necessary to study in detail the critical exponents associated with transition.

Also, perovskites attracted considerable interest due to their potential applications in solid oxide fuel cell (SOFC) cathodes, oxygen separating membranes, read heads in modern hard disk devices, and chemical sensors for gases [15–18]. In addition to their CMR and MCE, these oxides exhibit several important characteristics such as charge ordering, orbital ordering, isotope effect, etc. [19–21]. These effects were attributed to Mn\(^{3+}/Mn^{4+}\) mixed-valence state of the oxides, and as a consequence, a large number of studies were devoted to La-manganites with La ions substituted by rare earth or alkaline earth ions and Mn ions substituted by 3d-transition metal ions [22, 23]. Due to the similarity of the ionic radii of Mn\(^{3+}\) (0.65 Å) and Fe\(^{3+}\) ions (0.645 Å), Fe\(^{3+}\) ions substitute Mn\(^{3+}\) ions in six-fold octahedrally coordinated sites [24]. Accordingly, the substitution of Fe\(^{3+}\) for Mn\(^{3+}\) is not expected to modify the tolerance factor and, therefore, the Jahn-Teller distortion effect can be neglected. However, the deformation of the local structure in manganites which exhibit such distortions can be investigated by Mössbauer spectroscopy, which is an effective technique to examine deviations from octahedral symmetry at the Fe sites [25]. On the other hand, MCE in these oxides is defined by the adiabatic temperature change (\(\Delta T_{ad}\)) or the isothermal magnetic entropy change (\(\Delta S_M\)), which is a function of both magnetic field and temperature. Generally speaking, there are three principal methods to evaluate MCE [26]. First, by direct measurement of the adiabatic temperature change (\(\Delta T_{ad}\)), which is carried out by exposing the thermally insulated sample to a magnetic field. The second method is based on Maxwell’s relation, and \(\Delta S_M\) is calculated from magnetization measurements, and the third method is based on heat capacity measurements in zero-field cooled (ZFC) and field cooled (FC) processes [27–29].

The scenarios for tailoring of manganites with modified magnetic properties for specific applications included the adoption of different synthesis techniques to control the grain size and morphology of the produced ceramic, the variations of the stoichiometry of the starting powders and the experimental conditions, and the substitutions for the metal ions in the standard compound [30–33].

These issues are addressed briefly in the following sections. Further, we dedicated forthcoming sections to the presentation and discussion of our findings concerning the structural, magnetic and magnetocaloric properties of La-based manganites with La partially substituted by Ba and Sr, and Mn by Fe.
2. Sample preparation

Samples of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.0, 0.1, 0.2, 0.3$ and $1.0$) were prepared by the conventional ceramic method. This method is widely used for commercial production of powder. This technique, however, could be ineffective in controlling the grain size and morphology of the powder product. The synthesis of manganites powders by the various techniques often involved variations of the experimental conditions to determine the optimal conditions for the production of highly pure, high quality powder. Among others, the main factors taken into consideration in synthesizing the powders included: heat treatment, chemicals used in the starting powders, and stoichiometry of the precursor powder.

Powder samples were prepared by mixing metal oxides and carbonates (like La$_2$O$_3$, BaO, SrCO$_3$, MnCO$_3$ and (Fe$_2$O$_3$·H$_2$O) up to 99.9% purity) in proportions consistent with the stoichiometry of the samples. The starting materials were intimately mixed in an agate mortar, and heated in air at 900 °C for 10 h and slowly cooled to room temperature, and then sintered at 1000°C for 12 h. The obtained powder mixture was pressed in the form of pellets and sintered at 1200 °C for 50 h. Finally, these pellets were sintered at 1400 °C for 4 h.

3. Characterization techniques for the samples

The phase purity of the final product was examined by X-ray diffraction technique using Siemens D5000 X-ray diffractometer, with Cu-K$_\alpha$ radiation ($\lambda = 1.5405$ Å). The XRD data were also used for refining the lattice parameters by means of Rietveld analysis [34] using FULLPROF program software. The surface morphology and elemental analysis of our samples were evaluated respectively by scanning electron microscopy (SEM) imaging and the energy dispersive X-ray spectroscopy (EDX) facility available in (JEOL 840 A) electron microscope. The magnetization measurements versus temperature in the range 5 –500 K, and the isothermal magnetization curves in an applied magnetic field of up to 6 T were obtained using the SQUID (BS2 Quantum Design) facility at Louis Néel Laboratory of Grenoble. Isothermal curves around the ferromagnetic ordering transition temperature ($T_C$) of the samples were obtained in different steps. The low-temperature magnetic hysteresis loops of the samples were recorded under an applied magnetic field ranging from 0 to 6 T. The MCE was calculated from the magnetization measurements versus applied magnetic field up to 5 T at various temperatures.
4. Effects of substitution for La and Mn

4.1 Crystal structure

X-ray powder diffraction (XRD) measurements for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.0$, 0.1, 0.2, 0.3 and 1.0) samples were carried out at room temperature and Rietveld refinement of the XRD patterns are shown in Fig. 1 (a-e). XRD analysis indicates that all samples, except that with $x = 0.2$ and 1.0 consist of an orthorhombic single-phase with $P_{nma}$ space group. The weak diffraction peak at $2\theta = 31.53^\circ$ for the sample with $x = 0.2$ is due to the precipitation of a very small amount of Mn$_3$O$_4$ (see Fig. 1c) which is consistent with previously reported results [35, 36]. However, the sample with $x = 1.0$ contained small amounts of additional phases. The weak diffraction peaks at $2\theta = 28.0^\circ$ and $34.3^\circ$ correspond to the precipitation of a very small amount of (Ba, Sr)Fe$_2$O$_4$ spinel phase, while the weak diffraction peaks at $2\theta = 25.4^\circ$, $33.0^\circ$ and $53.6^\circ$ are consistent with the precipitation of a very small amount of $\alpha$-Fe$_2$O$_3$ (see Fig. 1e). Rietveld refinement of the X-ray powder data confirmed the presence of these minor phases, and the good agreement between the observed and calculated inter-planer spacing for the perovskite major phase is coherent with the value of the Goldschmidt tolerance factor $t_G$:

$$t_G = \frac{r_A + r_O}{\sqrt{2(r_B + r_O)}}$$  \hspace{1cm} (1)

Here $r_A$, $r_B$ and $r_O$ are respectively the average ionic radii of the A and B perovskite sites and oxygen anion [37].

Rietveld refinement of the X-ray powder data was carried out to determine the lattice parameters, unit cell volume, and atomic positions of all samples using the FULLPROF code [34].

Table 1 shows the refined unit cell parameters for all samples and unconstrained refinement of the data gave good values of $R_f$ and $\chi^2$ parameters. The results of the refined structural parameter for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.0$, 0.1, 0.2, 0.3 and 1.0) are summarized in Table 2. The structural analysis indicated that La/Ba/Sr ions were located at 4c ($x$, 0.25, $z$) position, Mn/Fe ions at 4b (0, 0, 0.5), and oxygen ions occupied two different sites, namely O$_1$ at 4c ($x$, 0.25, $z$) and O$_2$ at 8d ($x$, $y$, $z$) positions. It is noticed that the lattice parameters and the unit cell volume increased significantly only upon complete substituting manganese by iron. However, the volume and lattice parameters should be essentially independent of the Fe content due to the similarity of the radii of Mn$^{3+}$ and Fe$^{3+}$ ions in the octahedral sites as indicated by the constancy of the average tolerance factor $t_G$ (see Table 2). We can therefore associate this increase of the
lattice parameters and cell volume with the distortion of the original crystal lattice structure, and the adjustment of the Mn-O bond length and Mn-O-Mn bond angles. Our results are nearly comparable to those obtained by Jonker et al. [24] and Kallel et al. [38].

Fig. 1. Rietveld refinement of the XRD patterns of all elaborated samples.
Table 1. Cell parameters, unit cell volume and Curie temperature of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ (x = 0.0, 0.1, 0.2, 0.3 and 1.0) samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
<th>$T_C$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$_{0.11}$MnO$_3$</td>
<td>5.49299</td>
<td>7.79671</td>
<td>5.52697</td>
<td>236.70</td>
<td>345</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$<em>{0.11}$Mn$</em>{0.9}$Fe$_{0.1}$O$_3$</td>
<td>5.49824</td>
<td>7.79275</td>
<td>5.53661</td>
<td>237.22</td>
<td>190</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$<em>{0.11}$Mn$</em>{0.8}$Fe$_{0.2}$O$_3$</td>
<td>5.48432</td>
<td>7.81047</td>
<td>5.53495</td>
<td>237.09</td>
<td>130</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$<em>{0.11}$Mn$</em>{0.7}$Fe$_{0.3}$O$_3$</td>
<td>5.49878</td>
<td>7.80175</td>
<td>5.53985</td>
<td>237.66</td>
<td>80</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$_{0.11}$FeO$_3$</td>
<td>5.55271</td>
<td>7.85943</td>
<td>5.53789</td>
<td>241.68</td>
<td></td>
</tr>
</tbody>
</table>

The average crystallite size ($D_{xrd}$) was estimated from the XRD data using the Scherer relation [40] as shown in Eq.2.

$$D_{xrd} = \frac{k \lambda}{\beta \cos \theta}$$ (2)

Where $K$, $\lambda$, $\beta$, and $\theta$ are the grain shape factor, the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak, and the Bragg diffraction angle, respectively. The values of the effective crystallite sizes are summarized in Table 2. It is evident that the crystallite sizes of the samples were similar, with the exception of that with $x = 0.2$ which exhibited a better degree of crystallinity.

"Diamond" program was used to draw the unit cell (Fig. 2) and determine the distances between Mn ions and the nearest neighbor oxygen ions.

![Fig. 2. Crystal structure of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$MnO$_3$ and the coordination polyhedron on Mn.](image-url)
The $P_{nma}$ structure of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ at room temperature is evident, and although the MnO$_6$ octahedral are almost regular, they are slightly distorted as observed in a previous work [40]. The interatomic distances and Mn–O–Mn angles for the La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ samples, in the orthorhombic structure, are listed in Table 3.

Table 2. Refined structural parameter for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.0, 0.1, 0.2, 0.3$ and $1.0$), and the numbers in subscript represent the error bars.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$x = 0.0$</th>
<th>$x = 0.1$</th>
<th>$x = 0.2$</th>
<th>$x = 0.3$</th>
<th>$x = 1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La/Ba</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.00501</td>
<td>-0.00038</td>
<td>0.00815</td>
<td>0.00594</td>
<td>0.01771</td>
</tr>
<tr>
<td>y</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>z</td>
<td>0.00521</td>
<td>0.00295</td>
<td>0.00447</td>
<td>-0.00565</td>
<td>-0.00484</td>
</tr>
<tr>
<td>Mn/Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0</td>
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<tr>
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<td>0</td>
</tr>
<tr>
<td>z</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>O$_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.48283</td>
<td>0.47779</td>
<td>0.48975</td>
<td>0.48456</td>
<td>0.48989</td>
</tr>
<tr>
<td>y</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>z</td>
<td>-0.00521</td>
<td>0.02663</td>
<td>-0.02111</td>
<td>-0.00252</td>
<td>0.02259</td>
</tr>
<tr>
<td>O$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.25557</td>
<td>0.26318</td>
<td>0.26795</td>
<td>0.25934</td>
<td>0.27292</td>
</tr>
<tr>
<td>y</td>
<td>-0.00245</td>
<td>0.01423</td>
<td>-0.02998</td>
<td>-0.02098</td>
<td>0.02935</td>
</tr>
<tr>
<td>z</td>
<td>0.77323</td>
<td>0.76292</td>
<td>0.76104</td>
<td>0.77377</td>
<td>0.74165</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.43</td>
<td>1.52</td>
<td>1.57</td>
<td>1.38</td>
<td>1.33</td>
</tr>
<tr>
<td>$t_G$</td>
<td>0.9253</td>
<td>0.9255</td>
<td>0.9257</td>
<td>0.9259</td>
<td>0.9268</td>
</tr>
<tr>
<td>$D_{hkl}$ (nn)</td>
<td>28.11</td>
<td>29.02</td>
<td>69.15</td>
<td>31.45</td>
<td>35.12</td>
</tr>
</tbody>
</table>

Table 3. Interatomic distance and angles for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.0, 0.1, 0.2, 0.3$ and $1.0$) samples.

<table>
<thead>
<tr>
<th>Distances</th>
<th>$x = 0.0$</th>
<th>$x = 0.1$</th>
<th>$x = 0.2$</th>
<th>$x = 0.3$</th>
<th>$x = 1.0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn–O$_1$ (Å)</td>
<td>1.95</td>
<td>1.96</td>
<td>1.96</td>
<td>1.95</td>
<td>1.97</td>
</tr>
<tr>
<td>Mn–O$_2$ (Å)</td>
<td>1.84</td>
<td>1.85</td>
<td>1.85</td>
<td>1.83</td>
<td>1.92</td>
</tr>
<tr>
<td>Mn–O$_{22}$ (Å)</td>
<td>2.06</td>
<td>2.05</td>
<td>2.07</td>
<td>2.09</td>
<td>2.03</td>
</tr>
<tr>
<td>Angles</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn–O$_1$–Mn (°)</td>
<td>174.2</td>
<td>168.8</td>
<td>172.4</td>
<td>174.9</td>
<td>172.1</td>
</tr>
<tr>
<td>Mn–O$_2$–Mn (°)</td>
<td>175.8</td>
<td>173.5</td>
<td>166.1</td>
<td>169.82</td>
<td>164.8</td>
</tr>
</tbody>
</table>
4.2 Scanning electron microscopy investigation

Scanning Electron Microscopy (SEM) was employed to examine surface morphology of the La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ samples ($x = 0, 0.1, 0.2, 0.3$ and $1.0$) and SEM images of all samples are shown in Fig. 3 (a-e). Micrographs of all samples show that agglomerated particles are generally parallelepipedal with a homogeneous microstructure, fine granulation and porous structure. We estimated the average grain size by SEM based on the average grain size of ten different grains and then compared with those calculated by the Deby-Scherrer formula using data of X-ray diffraction. The size of the grains observed by SEM are greater than those calculated by the Scherrer formula; this can be explained by the fact that each particle observed by SEM is composed of several crystallites [42].

The chemical composition of the samples was estimated from the elemental analysis using energy dispersive X-ray spectra (EDX). Fig. 4 shows XRD spectra for all samples. The observed energy peaks correspond to the various elements in the samples. The obtained chemical composition of the samples was found close to the nominal chemical stoichiometry of the starting powders.

Fig. 3. Typical scanning electron micrographs (SEM images) of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ samples; (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ and, (e) $x = 1.0$. 
Fig. 4. EDX analysis spectral at room temperature of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ samples; (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$ and, (e) $x = 1.0$.

4.3 Magnetism

Fig. 5 shows the magnetization of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O ($x = 0.0$, 0.1, 0.2, 0.3 and 1.0) as a function of temperature for an applied field of 0.05 T. The samples with $x = 0$, 0.1 and 0.2 exhibited ferromagnetic (FM) to a paramagnetic (PM) phase transition as the temperature increased. Curie temperature ($T_C$) for each sample was determined from the minimum of $dM(T)/dT$ at the inflection point of the thermomagnetic curve, and the results are listed in Table 1. It is clear that $T_C$ could be determined for $x = 0.0$, 0.1, 0.2 and 0.3, which indicates that the level of substitution of manganese by iron in these samples does not destroy the ferromagnetic behavior below a temperature which is sensitive to the value of $x$ [43].
Further, $T_C$ for the un-substituted sample was found to be above room temperature, while even a low level of the substitution lowers $T_C$ to below room temperature. The observed decrease in magnetization and $T_C$ with increasing $x$ could be associated with the fact that Fe$^{3+}$ ions do not participate in the ferromagnetic double exchange (DE) interaction with Mn$^{3+}$ ions, but encourage the antiferromagnetic Fe$^{3+}$–O–Mn$^{3+}$, Mn$^{4+}$–O–Fe$^{3+}$ and Fe$^{3+}$–O–Fe$^{3+}$ super-exchange (SE) interactions [32]. With regard to the sample with $x = 0.3$, the magnetization exhibited a cusp at about 50 K. Such a behavior is typical of spin-glasses due to the competition between ferromagnetic (DE) and antiferromagnetic (super-exchange) interactions [44, 45]. Finally, the sample with $x = 1.0$ exhibited paramagnetic behavior down to the lowest temperature in this study, as expected for such iron oxides.

In order to better understand the magnetic properties of the samples, room temperature hysteresis loops were recorded in an applied magnetic field up to 1 T. Fig. 6 (a) shows that the magnetization for the un-substituted sample is almost saturated (52 A.m$^2$/kg) at 1 T applied magnetic field. This result is consistent with the thermomagnetic results which indicated that this sample is ferromagnetic at room temperature. However, the rest of the samples ($x = 0.1, 0.2, 0.3$ and $1.0$) magnetization curves at room temperature did not saturate in magnetic fields up to 1T (Fig. 6(b)). Further, it was observed that the increased level of iron substitution resulted in a significant drop in the spontaneous magnetization, which is associated with the weakening of the Mn$^{3+}$–Mn$^{4+}$ DE interactions. The magnetization curves for all samples demonstrated paramagnetic behavior. This is also

![Graph showing temperature dependence of magnetization](image-url)
consistent with the thermomagnetic results that $T_C$ for all substituted samples, if any, is below room temperature. The variation in the magnetic behavior with increasing Fe substitution level is due to the progressive weakening of the net (DE) interaction due to the decrease in number of Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ bonds [42-45]. The small hysteresis loop for the samples with $x = 0.2$ and 0.3 could be due to the presence of about 1 % of magnetically ordered phases, which reflects the presence of a small degree of inhomogeneity in the magnetic structure in these samples.

![Graph](image_url)

**Fig. 6(a).** Magnetization versus applied magnetic field at room temperature for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$MnO$_3$, (b) Magnetization versus applied magnetic field at room temperature for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.1$, 0.2, 0.3 and 1).

The magnetization curves $M(H)$ at $T = 5$ K are shown in Fig. 7. The samples with $x = 0$ and 0.1 were obviously ferromagnetic at this temperature and almost saturated at an applied field of 6 T. The saturation magnetizations for these samples are about 90 and 70 A.m$^2$/kg, respectively. However, the curves of the samples with higher $x$ values did not show saturation up to 6 T, which could be due to the increased SE antiferromagnetic coupling and the decreased DE ferromagnetic coupling with increasing Fe concentration, the competition between which could lead to frustration and the development of the spin-glass state [44-46]. The saturation magnetizations for these samples were determined from the low-of-approach to saturation in the high-field range, and found to be 54 and 29 A.m$^2$/kg for the samples with $x = 0.2$ and 0.3, respectively (Fig. 7–insets).
Fig. 7. Magnetization versus applied magnetic field at 5K for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{1-x}Fe_xO_3$ ($x = 0.0, 0.1, 0.2, 0.3$ and $1.0$). The insets show the fitting of isothermals curves corresponding respectively for each sample with $x = 0.2$ and $x = 0.3$.

### 4.4 Critical behavior

The experimental investigations of the critical behavior of manganites near the PM–FM phase transition using a variety of techniques provided a wide range of values for the magnetization critical exponent $\beta$ which embraces the mean field, short-range isotropic 3D-Heisenberg, and 3D-Ising model estimates [49–51]. The critical behavior was first described within the long-range mean-field theory applied to the DE model [6, 52-54]. However, evidence that the FM–PM transition in CMR manganites should belong to the 3D-Heisenberg universality class was reported [59, 50, 55, 56]. Further, the interpretations of a few relevant experimental results concerning the critical exponents and the universality class of manganites are still controversial [47, 49, 51, 56].

In this study, we conducted a study of the critical behavior of the $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{1-x}Fe_xO_3$ ($x = 0.0, 0.1, 0.2$) manganites by analyzing the critical exponents using different models, such as the modified Arrott plot (MAP) and the Kouvel–Fisher method, with the intention of understanding the magnetic interactions in these manganites. Based on the determined critical parameters $\beta$, $\gamma$, and $\delta$ we concluded that the critical phenomena near the PM–FM transition in these perovskites are best described by the 3D-Heisenberg model.
For this, we used vibrating sample magnetometer (BS2 magnetometer developed in Louis Neel Laboratory of Grenoble, France). The sensitivity of the magnetometer is better than $3 \times 10^{-7}$ Am$^2$. The system is capable of providing measurements of magnetization in the temperature range between 1.5 and 300 K, where the temperature of the sample is regulated by a circulating helium gas temperature. The maximum applied magnetic field used in this study was 5 T. Isothermal magnetic curves were obtained in a temperature range around the critical temperature in steps of 2 K.

The scaling hypothesis provides a model for characterizing a second-order phase transition by the values of the critical exponent’s $\beta$, $\gamma$, and $\delta$ associated with the spontaneous magnetization, the initial magnetic susceptibility, and the critical magnetization isotherm, respectively [48–50, 55-57]. In terms of these exponents, the magnetic parameters are given by the following relations:

- Below $T_C$, the spontaneous magnetization in the limit of zero-applied field is given by Eq. (3) as:

$$M_s(T) = M_0(-\varepsilon)^\beta \quad T < T_C$$

(3)

- Above $T_C$, the initial susceptibility is given by Eq. (4) as:

$$x_0^{-1} = \frac{h_0}{M_0} \varepsilon^\gamma \quad T > T_C$$

(4)

- At $T_C$, the dependence of the magnetization $M$ on the magnetic field $H$ is given by Eq. (5) as:

$$M = DH^{1/\delta} \quad T = T_C$$

(5)

Where, $\varepsilon = (T-T_C)/T_C$ is the reduced temperature, and $M_0$, $h_0$, and $D$ are the critical amplitudes.

The reliability of the critical exponents can be confirmed with the aid of the scaling theory. According to the scaling hypothesis, the magnetic equation of state in the critical regime obeys the scaling relation [48, 58]:

$$M(H, \varepsilon) = |\varepsilon|^\beta f_{\pm}(\frac{H}{|\varepsilon|^{\beta+\gamma}})$$

(6)
In this last equation, the (+) and (−) signs refer to \( T > T_C \) and \( T < T_C \), respectively.

Accordingly, the scaled magnetization isotherms \( M/\varepsilon^\beta \) plotted against \( H/\varepsilon^{\beta+\gamma} \) with the right choice of \( \beta, \gamma, \) and \( \delta \) values will fall onto two universal curves: one above \( T_C \) and another below \( T_C \). This is an important criterion for the determination of accurate and unambiguous values of the critical exponents.

Fig. 8 shows the isothermal magnetization curves (upper three panels) and Arrott plots (lower three panels) for the \( \text{La}_{0.67}\text{Ba}_{0.22}\text{Sr}_{0.11}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) samples in the temperature ranges 320–360 K for \( x = 0.0 \), 175–225 K for \( x = 0.1 \) and 100–150 K for \( x = 0.2 \), which are ranges around the Curie temperatures for the different samples. The Arrott plots \( M^2 \) vs. \( \mu_0H/M \) in Fig. 8 are nonlinear and exhibit an upward curvature even at high fields, indicating that the phase transitions in these samples do not satisfy the mean-field theory. Moreover, the concave downward curvature clearly indicates a second-order phase transition according to the criterion suggested by Banerjee [59]. In general, in the high-field region, the effects of charge, lattice, and orbital degrees of freedom are suppressed in a FM phase and the order parameter can be identified with the macroscopic magnetization. Thus, the magnetic phase transition in \( \text{La}_{0.67}\text{Ba}_{0.22}\text{Sr}_{0.11}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) (\( x = 0.0, 0.1, 0.2 \)) is a second-order transition. The nonlinearity of Arrott plots makes it difficult to evaluate the saturation magnetization, susceptibility, and critical temperature by extrapolation.
Fig. 8. Isothermal magnetization curves (upper three panels), and Arrott plots (lower three panels) at different temperatures for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$. (a). $x = 0$, (b). $x = 0.1$ and, (c). $x = 0.2$. 
Arrott and Noakes suggested a powerful method, the MAPs, to analyze the magnetic data sing the following empirical relation [60]:

\[
\left(\frac{H}{M}\right)^{\frac{1}{\gamma}} = \frac{T - T_C}{T_1} + \left(\frac{M}{M_1}\right)^{\frac{1}{\beta}}
\]  

(7)

Where \( T_1 \) and \( M_1 \) are material-dependent (the mean-field theory values of \( \beta = 0.5 \) and \( \gamma = 1 \) generate the regular Arrott plots). A linear relation between \( M_1^{1/\beta} \) and \( (H/M)^{1/\gamma} \) can then be sought by a proper choice of \( \beta \) and \( \gamma \). Thus, by choosing the critical parameters of a given universality class, a linear relation means that the compound belongs to that class.

Fig. 9. Standard Arrot plot (a), and modified Arrott plots with 3D-Heisenberg model (b), tricritical mean-field model (c), and 3D-Ising model (d) for \( \text{La}_{0.67}\text{Ba}_{0.22}\text{Sr}_{0.11}\text{MnO}_3 \) compound.
Fig. 9 shows the MAPs derived from the sets of critical parameters corresponding to the four different models:

- panel (a) the mean-field model ($\beta = 0.5, \gamma = 1$);
- panel (b) the 3D-Heisenberg model ($\beta = 0.365, \gamma = 1.336$);
- panel (c) the 3D-Ising model ($\beta = 0.325, \gamma = 1.24$),
- panel (d) the tri critical mean-field model ($\beta = 0.25, \gamma = 1$).

The positive slope of the curves indicates second-order phase transition [59]. Further, with the exception of the tri critical model, all models gave quasi-straight lines which are nearly parallel in the high-field region. Thus, it is not obvious which model best represents the actual critical exponents for the samples.

Accordingly, in order to select the model which best describes this system we calculated their relative slopes (RS) defined as $RS = S(T)/S(T_C)$. Then, the most adequate model should be the one that possesses an RS value which is very close to unit. Fig. 10 shows the RS vs. $T$ curves derived from the MAPs in Fig. 9 for the compound with $x = 0.0$. It is obvious that 3D-Heisenberg model is the best model which can describe this sample (La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$MnO$_3$). However, similar analysis (not shown) indicated that the behavior of the sample La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ is best described by 3D-Ising model.

The values of $\beta$ and $\gamma$ were then refined using Kaul’s method [61]. In this method, the high-field quasi-straight lines obtained with the initial values of $\beta$ and $\gamma$ in the MAP (Fig. 9) were extrapolated to intercept the vertical and horizontal axes at $M_S^{1/\beta}$ in the FM regime and $\chi^{-1/\gamma}$ in the PM regime, respectively. The critical isotherm passing through the origin determines $T_C$. Consequently, $M_S(T)$ and $\chi_0^{-1}(T)$ were evaluated and plotted against temperature, and fitted with Eqs. (8) and (9) to obtain new values of $\beta$ and $\gamma$ which were used to construct new MAPs.
In Fig. 11, we plotted the temperature dependence of $M_S(T)$ and $\chi_0^{-1}(T,0)$ for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0, 0.1, 0.2$). Table 4 shows the results of the fits. The values of the critical parameters for the sample with $x = 0.0$ seem to agree with the 3D-Heisenberg model.

Upon doping with Fe$^{3+}$, the critical exponent $\beta$ decreased and approached the value corresponding to the 3D-Ising model (see Table 4), while the critical exponent $\gamma$ increased slightly. Accordingly, we may conclude that the samples with $x = 0.1$ and 0.2 seem to qualitatively agree with the 3D-Ising model. Other workers [55] observed similar results and argued that their critical exponents are between those of the 3D-Heisenberg model and those of the mean-field model, and concluded the possibility of short range to long-range order crossover in their samples.
Fig. 11. Spontaneous magnetization $M_S$ and the inverse of the initial susceptibility $\chi_0^{-1}$ vs. temperature for $\text{La}_{0.67}\text{Ba}_{0.22}\text{Sr}_{0.11}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3$ with (a) $x = 0$, (b) $x = 0.1$, and (c) $x = 0.2$. 
Fig. 12. Kouvel–Fisher plots of $M_S(T)\frac{dM_S(T)}{dT}^{-1}$ and $\chi_0^{-1}(T)\frac{d\chi_0^{-1}(T)}{dT}^{-1}$ vs. temperature for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{1-x}Fe_xO_3$ with (a). $x = 0$, (b). $x = 0.1$ and, (c). $x = 0$. 
A more accurate method to determine the critical exponents $\beta$ and $\gamma$ is by the Kouvel–Fisher (KF) method [62]:

$$\frac{M_s(T)}{(dM_s(T)/dT)} = \frac{T-T_C}{\beta}$$  \hspace{1cm} (8)

$$\frac{\chi_0^{-1}(T)}{(d\chi_0^{-1}(T)/dT)} = \frac{T-T_C}{\gamma}$$  \hspace{1cm} (9)

According to this method, plots of $M_s(T)[dM_s(T)/dT]^{-1}$ vs. $T$ and $\chi_0^{-1}(T)[d\chi_0^{-1}(T)/dT]^{-1}$ vs. $T$ should yield straight lines with slopes of $1/\beta$ and $1/\gamma$, respectively, and the intercepts on the $T$ axes are equal to $T_C$. The linear fitting to the plots following the KF method for La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ give $\beta$, $\gamma$, and $T_C$ for $T < T_C$ and $T > T_C$ (See Fig. 12, Table 4).

The exponent $\delta$ can be directly obtained by plotting the critical isothermal magnetization curve on a log–log scale according to Eq. 10 (Fig. 13). The high-field region of the data is fitted by a straight line with a slope of $1/\delta$. The results of the analysis are shown in Table 1. Further, the exponents derived from static scaling analysis are related by the Widom scaling relation [63]:

$$\delta = 1 + \frac{\gamma}{\beta}$$  \hspace{1cm} (10)

Using this relation and the estimated values of $\beta$ and $\gamma$, we obtained $\delta$ values (see Table 4), which are very close to the estimates of $\delta$ from the critical isotherms at $T_C$. Thus, the estimates of the critical exponents are consistent.
Fig. 13. $M$ vs. $H$ on a log–log scale at several temperatures close to $T_C$ for the samples with (a). $x = 0$, (b). $x = 0.1$, and (c). $x = 0.2$. The straight line is the linear fit following Eq. 3 at $T \sim T_C$. 

$T_C = 342K$ $\delta = 4.73 \pm 0.04$ 

$T_C = 190K$ $\delta = 4536$
The obtained values of the critical exponents can be verified with the prediction of the scaling theory in the critical region using Eq. 4. Fig. 14 shows plots of $M|\varepsilon|^{\beta}$ vs. $H|\varepsilon|^{\left(\beta+\gamma\right)}$ for the three samples. The Fig. 14 demonstrates two different branches, one for temperatures below $T_C$ and the other for temperatures above $T_C$. The inset shows the same data on a log–log scale. From this figure, it can be clearly seen that the scaling is well obeyed; all the points fall on the two branches. This indicates that the determined critical parameters are in good accordance with the scaling hypothesis.

The values of critical exponents of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ and the theoretical values based on various models are summarized in Table 4 for comparison. From Table 4, we can clearly see that the values of the critical exponents for the sample with $x = 0.0$ agree with those of the 3D-Heisenberg-like ferromagnet. This behavior is similar to that of other CMR manganites belonging to the universality of 3D isotropic ferromagnets with short-range exchange couplings [51]. However, with the substitution of Mn$^{3+}$ by Fe$^{3+}$, the critical exponent $\gamma$ decreased and approached the 3D-Ising $\gamma = 1.24$. On the other hand, the critical exponent $\beta$ increased to $\beta = 0.398$. This may indicate that the magnetic transition could still be described by short-range interactions (3D-Heisenberg/3D-Ising). However, the substitution of Fe$^{3+}$ results in breaking some of the Mn$^{4+}$–O$^{2−}$–Mn$^{3+}$ bonds in a random fashion, and a consequent suppression of the DE interaction and long-range FM order. This was demonstrated by the significant decrease of $T_C$ and saturation magnetization for Fe-substituted samples (Fig. 8, Table 4). Our results are nearly comparable to those obtained by Omri et al. [64]. In fact, we have found that the parent sample La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$MnO$_3$ exhibits a sharp FM–PM transition. As Fe-substitution increases it causes a decrease in the magnetization and the magnetic transition become increasingly broader. These results have been explained by the fact that, the substitution of the Mn$^{3+}$ by Fe$^{3+}$ Ions reduces the Mn$^{3+}$/Mn$^{4+}$ ratio, leading to a suppression of the DE interaction and enhancement of the super exchange interaction.

A similar behavior for manganites was reported by others authors [65, 66]. The broadening of the PM–FM transition was ascribed to magnetic inhomogeneity and the development of an AFM phase with increasing $x$. A significant degree of Fe$^{3+}$ substitution reduces the Mn$^{3+}$/Mn$^{4+}$ ratio significantly and weakens the DE interaction on the one hand, and increases the possibility of occurrence of Fe$^{3+}$–O$^{2−}$–Fe$^{3+}$ bonds and the subsequent AFM superexchange interaction. This may result in competition between ferromagnetism and antiferromagnetism, and lead to spin glass-like behavior at high levels of substitution as reported [65].
Fig. 14. Scaling plot $M|\varepsilon|^{-\beta} \times H|\varepsilon|^{-(\beta+\gamma)}$, indicating two universal curves below and above $T_C$ for $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{1-x}Fe_xO_3$ with (a) $x = 0$, (b) $x = 0.1$, and (c) $x = 0.2$. Insets we show the same plots on log-log scales.
The critical exponents of a homogeneous ferromagnet are governed by the lattice dimension (3D), dimension of the order parameter (n = 3, magnetization), and range of interaction (short range, long range, or infinite). Fisher et al. [67] performed a renormalization group analysis of systems with an exchange interaction of the form \( J(r) = 1/r^{d+\sigma} \) (d is the dimension of the system and \( \sigma \) is the range of the interaction). If \( \sigma < 3/2 \), the mean-field exponents are valid. The Heisenberg exponents are valid for \( \sigma > 2 \). For intermediate range, i.e., for \( J(r) \approx r^{-3-\sigma} \) with \( 3/2 < \sigma < 2 \) the exponents belong to a different universality class which depends upon \( \sigma \). In a general way, the evolution of the critical exponents tends to move toward the values of the mean-field theory with long-range interaction.

**Table 4. Comparison of the critical exponents of \( \text{La}_{0.67}\text{Ba}_{0.22}\text{Sr}_{0.11}\text{Mn}_{1-x}\text{Fe}_x\text{O}_3 \) \((x = 0, 0.1, 0.2)\) with earlier reports, and with the various theoretical models.**

<table>
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<th>Composition</th>
<th>Method</th>
<th>( T_c(K) )</th>
<th>( \beta )</th>
<th>( \gamma )</th>
<th>( \delta )</th>
<th>Ref.</th>
</tr>
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<td>( \text{La}<em>{0.67}\text{Ba}</em>{0.22}\text{Sr}_{0.11}\text{MnO}_3 )</td>
<td>M</td>
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<td>0.378±0.003</td>
<td>1.388±0.001</td>
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<td></td>
<td>A</td>
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<td>0.386±0.006</td>
<td>1.393±0.004</td>
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<td></td>
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<tr>
<td></td>
<td>Cl(exp)</td>
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<td></td>
<td></td>
<td>4.73±0.003</td>
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<tr>
<td></td>
<td>Cl(cal)</td>
<td></td>
<td></td>
<td></td>
<td>4.67±0.004</td>
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</tr>
<tr>
<td>( \text{La}<em>{0.67}\text{Ba}</em>{0.22}\text{Sr}<em>{0.11}\text{Mn</em>{0.9}Fe_{0.1}O}_3 )</td>
<td>M</td>
<td>190.64±0.11</td>
<td>0.398±0.002</td>
<td>1.251±0.005</td>
<td>[70]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>A</td>
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<td>1.247±0.003</td>
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<td></td>
<td>Cl(exp)</td>
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<td>4.53±0.002</td>
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<td>Cl(cal)</td>
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<td>4.14±0.007</td>
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<tr>
<td>( \text{La}<em>{0.67}\text{Ba}</em>{0.22}\text{Sr}<em>{0.11}\text{Mn}</em>{0.8}\text{Fe}_{0.2}\text{O}_3 )</td>
<td>M</td>
<td>130.24±0.12</td>
<td>0.411±0.001</td>
<td>1.241±0.004</td>
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<td></td>
<td>A</td>
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<td>( \text{La}<em>{0.75}\text{Sr}</em>{0.25}\text{Mn}<em>{0.9}\text{Ga}</em>{0.1}\text{O}_3 )</td>
<td>M</td>
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<td>1.221±0.002</td>
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<td>0.428±0.005</td>
<td>1.286±0.004</td>
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<td>( \text{La}<em>{0.9}\text{Ba}</em>{0.1}\text{Mn}<em>{0.85}\text{Fe}</em>{0.15}\text{O}_3 )</td>
<td>KF</td>
<td>158.24±0.01</td>
<td>0.370±0.02</td>
<td>1.359±0.02</td>
<td>4.67±0.01</td>
<td>[68]</td>
</tr>
<tr>
<td>( \text{La}<em>{0.9}\text{Ba}</em>{0.1}\text{Mn}<em>{0.8}\text{Fe}</em>{0.2}\text{O}_3 )</td>
<td>MAP</td>
<td>125±0.08</td>
<td>0.365±0.01</td>
<td>1.227±0.03</td>
<td>4.52±0.03</td>
<td>[68]</td>
</tr>
<tr>
<td>( \text{La}<em>{0.9}\text{Ba}</em>{0.1}\text{Mn}<em>{0.8}\text{Fe}</em>{0.2}\text{O}_3 )</td>
<td>KF</td>
<td>125.61±0.05</td>
<td>0.318±0.02</td>
<td>1.159±0.02</td>
<td>4.36±0.01</td>
<td>[68]</td>
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<td>( \text{La}<em>{0.9}\text{Sr}</em>{0.3}\text{MnO}_3 )</td>
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<td>354.0</td>
<td>0.37</td>
<td>1.22</td>
<td>4.25</td>
<td>[49]</td>
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<td>( \text{La}<em>{0.9}\text{Sr}</em>{0.3}\text{Mn}<em>{0.8}\text{Ti}</em>{0.2}\text{O}_3 )</td>
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<td>0.518</td>
<td>1.002</td>
<td>2.95</td>
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4.5 Magnetocaloric study

Magnetization measurements versus applied magnetic field up to 5 T were obtained at several temperatures below and above $T_C$ for the samples with $x = 0$, 0.1, and 0.2, and in the temperature range between 100 K and 300 K for the sample with $x = 1.0$. The isothermal curves (Fig. 8) indicated that the magnetization for the un-substituted sample in the ferromagnetic regime increased sharply and saturated at an applied field below 0.5 T. This behavior is characteristic for a soft magnetic material, and is consistent with the room temperature hysteresis behavior.

However, the curves for the substituted samples continued to rise and did not saturate even at 5 T. Fig. 8 shows $M^2$ vs. $(\mu_0 H / M)$ Arrott plots derived from the magnetization curves. The plots exhibited a positive slope around $T_C$ which confirms that our samples (with the exception of that with $x = 1.0$) exhibit second order ferromagnetic to paramagnetic phase transition [59, 71]. The plots for the sample with $x = 1$, demonstrated the absence of such transition.

In order to study the magnetocaloric properties of our samples, the temperature dependence of magnetic entropy change was evaluated (Fig. 15). The magnetic entropy change, $-\Delta S_M$, induced by the magnetic field change was calculated according to the classical thermodynamic theory based on Maxwell’s relations using the following equation according to [72]:

$$\Delta S_M (T)_{xH} = \int_{H_i}^{H_f} \left( \frac{\partial M (T, H)}{\partial T} \right)_{H} dH$$

(11)

The numerical integration of the latter formula gives the values of $\Delta S_M$ at different values of fields and temperatures:

$$\Delta S_M = \sum_i \frac{M_{i+1} - M_i}{T_i - T_{i+1}} \Delta H_i$$

(12)

Here $M_i(T, H)$ and $M_{i+1}(T_{i+1}, H)$ are the experimental values of magnetization measured at temperatures $T_i$ and $T_{i+1}$, respectively, under applied magnetic field $H_i$. Fig. 15(a) shows the temperature dependence of the magnetic entropy change ($-\Delta S_M$) vs. temperature for the un-substituted sample at different external applied magnetic fields of 1 to 5 T.

As expected, the magnetic entropy change enhanced with increasing applied magnetic field, and exhibited a maximum value around $T_C$. The magnitude of the maximum
entropy change increased from 0.675 J kg$^{-1}$ K$^{-1}$ at an applied field of 1 T to 2.258 J kg$^{-1}$ K$^{-1}$ at an applied field of 5 T.

Figs. 15 (b) and (c) show $-\Delta S_M$ of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0.1$ and $x = 0.2$) samples as a function of temperature at different external magnetic fields. The magnitude of the maximum change in magnetic entropy for the sample with $x = 0.1$ improved only slightly at high fields with respect to the un-substituted sample, and the peak became sharper around $T_C$. However, the maximum entropy changes for the sample with $x = 0.2$ dropped down to about half of the value for the previous two samples (1.03 J Kg$^{-1}$ at 139 K). This is due to the reduction in the rate of change in magnetization with increasing temperature as a result of the increase in the antiferromagnetically aligned moments of Mn and Fe ions. Our magnetic results are consistent with those obtained by P. Nisha et al. [73]. The small value of magnetic entropy change can be associated with the fact that the magnetic phase transition in these samples is of second order.

Generally, materials with first order transitions exhibit much larger magnetocaloric effect than materials with second order transitions. However, the importance of the studied system stems from the ability to tune their properties and control the structural and morphological factors, in addition to the ease of synthesizing such materials with good chemical stability. In Table5, we list the MCE values of the present compound in comparison with those reported in the literature having the same chemical elements.

The relative cooling power (RCP) was calculated using the formula:

$$RCP = |\Delta S_M^{MAX}(T,H)| \times \delta T_{FWHM}$$

Where $\delta T_{FWHM}$ is the full-width at half-maximum of $|\Delta S_M^{MAX}|$ versus temperature [74, 75]. Relatively high RCP values of 193.27 J/kg and 153.2 J/kg at $\Delta H = 5$ T were obtained for the samples $x = 0$ and $x = 0.1$. Despite the fact that iron doping reduces $T_C$ and $|\Delta S_M|$ at relatively high iron concentration, the observed properties of the investigated system are promising and open the way for investigations of materials useful for magnetic refrigeration.
Fig. 15. Temperature dependence of magnetic entropy change for samples: (a) $La_{0.67}Ba_{0.22}Sr_{0.11}MnO_3$, (b) $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.9}Fe_{0.1}O_3$, (c) $La_{0.67}Ba_{0.22}Sr_{0.11}Mn_{0.8}Fe_{0.2}O_3$. 
Table 5. MCE values of the compound in comparison with reported one in the literature having the same chemical elements.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\Delta S_M^{Max}$ (J kg$^{-1}$ K$^{-1}$)</th>
<th>RCP (J kg$^{-1}$)</th>
<th>$\Delta H$ (T)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd</td>
<td>9.5</td>
<td>410</td>
<td>5</td>
<td>[76]</td>
</tr>
<tr>
<td>Gd$_5$(Si$_2$Ge$_2$)</td>
<td>18.5</td>
<td>535</td>
<td>5</td>
<td>[76]</td>
</tr>
<tr>
<td>La$<em>{0.8}$Ba$</em>{0.2}$MnO$_3$</td>
<td>4.15</td>
<td>230</td>
<td>5</td>
<td>[46]</td>
</tr>
<tr>
<td>La$<em>{0.8}$Ba$</em>{0.2}$Mn$<em>{0.95}$Fe$</em>{0.05}$O$_3$</td>
<td>3</td>
<td>238</td>
<td>5</td>
<td>[46]</td>
</tr>
<tr>
<td>La$<em>{0.8}$Ba$</em>{0.2}$Mn$<em>{0.9}$Fe$</em>{0.1}$O$_3$</td>
<td>2.62</td>
<td>211</td>
<td>5</td>
<td>[46]</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$_{0.11}$MnO$_3$</td>
<td>2.258</td>
<td>193</td>
<td>5</td>
<td>[77]</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$<em>{0.11}$Mn$</em>{0.9}$Fe$_{0.1}$O$_3$</td>
<td>2.261</td>
<td>153</td>
<td>5</td>
<td>[77]</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.22}$Sr$<em>{0.11}$Mn$</em>{0.8}$Fe$_{0.2}$O$_3$</td>
<td>1.03</td>
<td>91</td>
<td>5</td>
<td>[77]</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.33}$MnO$_3$</td>
<td>1.48</td>
<td>161</td>
<td>5</td>
<td>[78]</td>
</tr>
<tr>
<td>La$<em>{0.67}$Ba$</em>{0.33}$Mn$<em>{0.98}$Ti$</em>{0.02}$O$_3$</td>
<td>3.19</td>
<td>307</td>
<td>5</td>
<td>[79]</td>
</tr>
<tr>
<td>La$<em>{0.7}$Sr$</em>{0.3}$Mn$<em>{0.093}$Fe$</em>{0.07}$O$_3$</td>
<td>4</td>
<td>25</td>
<td>2</td>
<td>[79]</td>
</tr>
</tbody>
</table>

Conclusions

We investigated the structural, magnetic and magnetocaloric properties of nanopowder samples La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{1-x}$Fe$_x$O$_3$ ($x = 0, 0.1, 0.2, 0.3$, and $1.0$) prepared by the conventional ceramic method. By Rietveld refinement, we generally found that all samples were almost single-phase and crystallize in the orthorhombic structure with $Pnma$ space group. However, a weak diffraction peak corresponding to a very small amount of Mn$_3$O$_4$ precipitates was identified in the pattern of the sample with $x = 0.2$. The substitution of Mn by Fe was found to influence the magnetic characteristics significantly as a result of the development of SE interactions at the expense of the ferromagnetic interactions. Relatively large values of MCE were obtained at low Fe substitution levels, and $\Delta S_M^{Max}$ reached the highest value for the sample with $x = 0.1$ at an applied magnetic field of 5 T.

The critical behavior of La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$MnO$_3$, La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ and La$_{0.67}$Ba$_{0.22}$Sr$_{0.11}$Mn$_{0.8}$Fe$_{0.2}$O$_3$ perovskites was comprehensively studied by the isothermal dc-magnetization around the Curie point $T_C$. Refined values of the parameters $T_C$, $\beta$, $\gamma$, and $\delta$ were obtained by means of the MAP and Kouvel–Fisher methods. The values of critical exponents for the parent sample with $x = 0$ agree with those of a 3D-Heisenberg-like ferromagnet with short-range exchange couplings. However, with the
substitution of Fe$^{3+}$ ion, the critical exponent $\beta$ increased, and the critical exponent $\gamma$ decreases approaching the 3D-Ising value of $\delta = 1.24$. These results show a change in the universality class of these manganites with iron doping, which can be explained by the suppression of the DE interaction caused by Fe$^{3+}$ ions at the Mn$^{3+}$ site, and the enhancement of the super exchange interaction. These findings indicated that the critical behavior of the magnetic transition in manganites is sensitive to Mn site doping.

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