We present a detailed study on the physical properties of La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ ($0 \leq x \leq 0.1$) type perovskites. Among these, ABO$_3$ compounds are known as perovskite manganites. These materials have a general formula Re$_{1-x}$A$_x$Mn$_2$O$_3$ ($0 \leq x \leq 0.1$) samples can be suggested for use in magnetic refrigeration technology above room temperature. The electrical resistivity ($\rho$) vs. temperature plots exhibit a transition from metallic behavior to semiconductor behavior in the vicinity of $T_{FM}$. The adiabatic small polaron hopping (ASPH) model is applied in the PM-semiconducting part ($T > T_{FM}$). Throughout the temperature range, $\rho$ is adjusted by the percolation model. This model is based on the phase segregation of FM-metal clusters and PM-insulating regions.

1. Introduction

Magnetic refrigeration (MR) technology based on the magnetocaloric effect (MCE) is advancing to become a suitable technology, compared to conventional gas refrigeration, due to a number of advantages. The MCE is generally characterized by two factors: change in entropy ($\Delta S_M$) and relative cooling power (RCP).

Gadolinium (Gd) is a pure lanthanide element and is the first material that has a high MCE with a Curie temperature ($T_C$) near room temperature ($RT$). Interestingly, further MCE investigations were performed for binary Gd–M compounds, such as Gd$_3$SiGe$_2$, which shows a MCE twice that of Gd. The researchers focused on finding new cheaper materials with larger MCEs. In this context, manganites with perovskite structure have certain advantages over Gd: their elements are not expensive, they are chemically stable, they have high resistivity and they exhibit a good MCE under low magnetic fields.

Among these, ABO$_3$ compounds are known as perovskite manganites. These materials have a general formula Re$_{1-x}$A$_x$Mn$_2$O$_3$ ($0 \leq x \leq 0.1$) samples can be suggested for use in magnetic refrigeration technology above room temperature. The electrical resistivity ($\rho$) vs. temperature plots exhibit a transition from metallic behavior to semiconductor behavior in the vicinity of $T_{FM}$. The adiabatic small polaron hopping (ASPH) model is applied in the PM-semiconducting part ($T > T_{FM}$). Throughout the temperature range, $\rho$ is adjusted by the percolation model. This model is based on the phase segregation of FM-metal clusters and PM-insulating regions.
transition close to $T_C$. Several studies have been performed on the magnetocaloric properties of this compound, which exhibits a large change in magnetic entropy, with a narrow range of working temperatures in the vicinity of $T_C$. In addition, several investigations have been carried out to estimate the substitution effects of the Mn site and these have shown that, for the La$_{1-x}$Sr$_x$MnO$_3$ family, even a low rate of substitution at the Mn site would induce a significant change in the properties of magnetotransport. The values of $T_C$ and $\Delta S_M$ are generally affected by the partial substitution of manganese ions by certain transition metals, for example the In ion, the Al ion, etc. On the other hand, the substitution of the rare earth La$^{3+}$ by certain metals lead to a significant change in the magnetic and electrical properties.

Indeed, the substitution of the Re site with divalent ions proves the oxidation of Mn$^{3+}$ to Mn$^{4+}$, which is the origin of the ferromagnetic character. The magnetic coupling between Mn$^{4+}$ and Mn$^{3+}$ is usually governed by the movement of the electron, for example between the two partly filled d layers with a strong Hund’s coupling on site.

The issue of replacing magnetic and non-magnetic ions in the Mn site is very important. For example, the partial substitution of Mn$^{3+}$ ions with Ni$^{2+}$ ions modifies the ratio of the Mn$^{4+}$–O$^-$–Mn$^{3+}$ network and leads to a decrease of the double exchange (DE) interactions. Several studies have been carried out to explain the relationship between the magnetotransport and magnetic properties of Re$_{1-x}$A$_x$MnO$_3$ substituted by different elements on the Mn site. Based on the information given in this article, we have carefully discussed the physical properties in La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ ($0 \leq x \leq 0.1$) compounds.

2. Experimental details

2.1 Preparation

The La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ ceramics were prepared using the sol-gel route. High purity precursors La(NO$_3$)$_3$·6H$_2$O, Sr(NO$_3$)$_2$·6H$_2$O, Mn(NO$_3$)$_2$·4H$_2$O, Ba(NO$_3$)$_2$ and Ni(NO$_3$)$_2$·6H$_2$O were weighed in stoichiometric proportions and then dissolved in distilled water with continuous stirring, whilst on a hot plate. The mixtures were dispersed in solutions containing a complexation agent (citric acid) and a polymerizing agent (ethylene glycol). The citric acid was used as a chelating agent and the ethylene glycol was used as a gelification agent. In order to form a homogenous yellowish gel, the solutions were heated on a hotplate at about 100 °C for 1 h under magnetic stirring. Then, to remove the excess solvent, the temperature was increased to 400 °C and the combustion led to a very fine and very homogeneous powder (black powder). At the end of this process, the calcinated powder was ground and pressed into pellets. The pellets were subjected to sintering at 900 °C for 24 hours in air.

2.2 Characterization

X-ray powder diffraction (XRD) was used to examine the structural behavior of the samples. Using a “Panalytical X’Pert Pro” diffractometer, the XRD was conducted through Cu-Kα radiation ($\lambda_{Cu} = 1.54056$ Å) with a 0.0167° step size and 19$^\circ \leq 2\theta \leq 90^\circ$ angular range. The refinement was analyzed by Rietveld’s program using FULLPROF software (version 0.2-March 1998-LLB-JRC). A Philips XL30 scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) spectrometer working at 15 kV were used to carry out a morphological study of the compounds. The magnetization measurements were recorded with a BSI and BS2 magnetometer, which was developed in the Louis Néel laboratory in Grenoble.

3. Results and discussion

3.1 X-ray analysis

The XRD patterns of the La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ (LBSMNO) samples, recorded at room temperature (RT), are presented in Fig. 1. The analysis of these spectra indicates that all the compounds were successfully prepared with a good crystallinity and a single phase of La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$; we have not detected a second phase. In the inset of Fig. 1, we show the crystalline structure of these samples. A good fit agreement between the simulation and the experimental pattern was observed.

The patterns of our samples were indexed in the rhombohedral (R3c) symmetry (no. 167), with (La, Ba, Sr): 6a (0, 0, 0.25), (Mn, Ni): 6b (0, 0, 0) and O: 18 (x, 0, 0.25). The different structural parameters are tabulated in Table 1. When the Ni substitution increases, the volume and the lattice parameters decrease. A similar behavior has also been previously observed.

This decrease is explained by the fact that the average ionic radius of the manganese site (0.599 ≤ $r_{Mn}^{Ni}$ ≤ 0.592) decreases, which can be assigned to the formulation of a higher level of Mn$^{3+}$, compared to Mn$^{3+}$.

Taking into account the neutrality of La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ ($0 \leq x \leq 0.1$) compounds, the XRD diagrams for solid solutions of the LBSMNO samples. Each of the peaks of these manganites are indexed in the rhombohedral structure. The inset shows the results of the Rietveld’s analysis of sample $x = 0.10$ as an example.

![Fig. 1](image-url)
Table 1 Structural parameters (X-ray Rietveld refinement) for the LBSMNO samples at RT

| $x$   | 0.000 | 0.050 | 0.100 |
|-------|-------|-------|-------|
| $\alpha$ (Å) | 5.4971(4) | 5.4824(3) | 5.4785(1) |
| $\varepsilon$ (Å) | 13.4713(5) | 13.4572(1) | 13.4491(3) |
| $V$ (Å$^3$) | 352.54(1) | 350.30(2) | 349.58(4) |
| ($\text{La}, \text{Sr}, \text{Ba}$)$_2$BO$_6$ (Å$^3$) | 0.83(2) | 0.54(3) | 0.48(3) |
| ($\text{Mn}/\text{Ni}$)$_2$BO$_6$ (Å$^3$) | 0.4472(1) | 0.4526(3) | 0.4435(5) |
| $q$ (%) | 7.26 | 7.32 | 7.35 |
| $p$ (%) | 2.42 | 3.51 | 4.11 |
| $\chi^2$ (%) | 2.62 | 3.50 | 2.17 |
| $D$ (nm) | 0.974 | 0.973 | 0.972 |
| $\theta$ (°) | 1.963(1) | 1.963(1) | 1.963(1) |
| $D_{\text{WH}}$ (°) | 0.286 | 0.285 | 0.283 |
| $W$ (arb. units) | 4.73 | 4.71 | 4.66 |
| $D_{\text{WH}}$ (µm) | 55 | 50 | 49 |
| $d_{\text{(Mn/Ni)-O}}$ (Å) | 166.2(1) | 164.98(9) | 162.82(6) |
| $d_{\text{eff}}$ (Å) | 1.9571(1) | 1.9587(2) | 1.9633(1) |
| $\theta_{\text{WH}}$ (°) | 1.13 | 1.12 | 1.11 |
| $\rho$ (%) | 7.26 | 7.32 | 7.33 |

whereas $d_{\text{eff}}$ increases, leading to a tilting of the $\text{BO}_6$ octahedrons.

The perovskite structure can be distorted from the ideal cubic structure, which greatly affects the properties. These distortions are principally given by the relationship between the ionic radius of the cations, defined by the tolerance factor $t_G$:

$$t_G = \frac{r_A + r_O}{2(r_B + r_O)}$$

where $r_A$ is the radius of the A site ions, $r_B$ is that of the B site ions and $r_O$ is the radius of the oxygen ions, which are found in the tables of Shannon. Generally, a perovskite exhibits a cubic structure if $t_G$ is equal to 1 and it undergoes distortions if $t_G$ deviates from 1.

In our work, the tolerance factor $t_G$ decreases with the increase of Ni (Table 2).

The rate of rhombohedral deformation $D\%$ can be calculated employing the expression: $D\% = \frac{1}{3} \sum_{\theta_i} \left( \frac{a_i - \pi}{\pi} \right) \times 100$, where

$$\theta_i = \left( \frac{a_1 a_2 a_3}{3} \right)^{\frac{1}{3}}, a_1 = a_2 = a$$

From Table 2, the value of $D$ decreases with the decrease in mean $r_{\text{Mn/Ni}}$.

On the other hand, the average crystallite size $D_{\text{SC}}$ can be calculated using Scherrer’s relationship:

$$D_{\text{SC}} = \frac{0.9 \times \lambda}{\beta \cos \theta}$$

Here, $\beta$ is the full width at half maximum (FWHM) of the peak (104), $\lambda$ represents the wavelength of the Cu-K$\alpha$ radiation ($\approx 1.54056$ Å) and $\theta$ corresponds to the angle of the most intense peak (104). The results are given in Table 2. It can be deduced that the grain size ($D_{\text{SC}}$) decreases from 55 to 49 nm when we introduce the Ni$^{2+}$ ions.

As in Scherrer’s method, the crystallite size values were determined from the Williamson–Hall equation:

$$\beta \cos \theta = \frac{K\lambda}{D_{\text{WH}}} + 4\varepsilon \sin \theta$$

$\theta$ is the Bragg angle, $\varepsilon$ is the strain and $D_{\text{WH}}$ is the crystallite size. The slope of the plot of $\beta \cos \theta$ (y-axis) vs. $4 \sin \theta$ (x-axis) gives the strain ($\varepsilon$) and the crystallite size ($D_{\text{WH}}$) can be calculated from the intercept of this line on the y-axis (Fig. 2). The calculated values are grouped in Table 2. We can deduce from this result that the average crystallite size determined by Williamson–Hall is greater than that obtained by Scherrer’s method, which is due to the broadening effect caused by the strain exhibited in this technique.

3.2 Morphological characterization

Fig. 3 presents the morphology of La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ ($x = 0$ and 0.1) as examples, demonstrated in the SEM images. It can be seen that the distribution of the grains is uniform over the entire surface and the grains are well joined, which shows that our samples are well formed.
ImageJ software was employed to determine a statistical count of the grain size, which was performed on the SEM images. This technique consists of measuring the diameters of all the particles in the SEM image. Then, we adjusted these data using the log-normal function.

\[
f(D) = \left( \frac{1}{\sqrt{2\pi\sigma D}} \right) \exp \left( -\frac{\ln^2(D/D_0)}{2\sigma^2} \right)
\]

Fig. 3  Typical SEM images for \( x = 0.00 \) and 0.10, (a) and (b) present the histograms of particle size and (c) shows the EDX analysis for \( x = 0.10 \).
Ba0.2Sr0.2Mn0.9Ni0.1O3 is presented in Fig. 3(c) as an example. We calculated the X-ray density, the lattice constant, and the average particle size. The particle size distribution was determined (Table 2).

This technique can be explained by the fact that each particle observed by SEM is made up of several crystallites. The energy dispersive X-ray microanalysis (EDX) spectrum of La0.6–Ba0.2Sr0.2Mn3+Ba0.2Sr0.2Mn3+Ni2+O3, shown in Fig. 3(c), is an example. This technique confirms the composition and purity of the samples. The EDX spectra reveal the homogeneous distribution of La, Ba, Sr, Mn, Ni and O atoms over a wide surface area.

To evaluate the porosity $p$ (%) we calculated the X-ray density $\rho = M/Na^3$, where $M$ is the molecular weight and $Na$ is Avogadro’s number$^{29}$ (see Table 2).

### Table 3: Transition temperature $T_C$, $\theta_{CW}$, $\mu_0\theta$, $\mu_0\mu_{exp}$ vs. of $x$ ratio for LBSMNO

| $x$ | $T_C$ (K) | $\theta_{CW}$ (K) | $\mu_0\theta$ | $\mu_0\mu_{exp}$ | $M_s$ (emu g$^{-1}$) | $M_i$ (emu g$^{-1}$) | $R$ |
|-----|-----------|-----------------|---------------|-----------------|------------------|------------------|-----|
| 0.00| 354       | 358             | 4.92          | 4.48            | 84               | 13               | 0.066 |
| 0.05| 320       | 326             | 4.77          | 4.34            | 79               | 8                | 0.10  |
| 0.10| 301       | 308             | 4.64          | 4.19            | 75               | 5                | 0.15  |

Where, $\sigma$ is the median diameter obtained from the data and $D_0$ is the median diameter obtained from the SEM images. Fig. 3(a) and (b) present the grain number (counts) versus the particle size. Using the fit results, the mean diameter

$$ (D) = D_0 \exp\left(\frac{\sigma^2}{2}\right) $$

and standard deviation $\sigma_D = (D)[\exp(\sigma^2) - 1]^{1/2}$ were determined (Table 2).

It is remarkable that the average size of the particles obtained is greater than the average size of the crystallites determined by XRD. This can be explained by the fact that each particle observed by SEM is made up of several crystallites. The energy dispersive X-ray microanalysis (EDX) spectrum of La0.6–Ba0.2Sr0.2Mn3+Ba0.2Sr0.2Mn3+Ni2+O3, shown in Fig. 3(c), is an example. This technique confirms the composition and purity of the samples. The EDX spectra reveal the homogeneous distribution of La, Ba, Sr, Mn, Ni and O atoms over a wide surface area.

To evaluate the porosity $p$ (%) we calculated the X-ray density $\rho = M/Na^3$, where $M$ is the molecular weight and $Na$ is Avogadro’s number$^{29}$ (see Table 2).

### 3.3 Magnetic properties

The evolution of $M(T)$ measured at 0.05 T in cooled zero field (ZFC) and cooled field (FC) modes is presented in Fig. 4. It is observed that, in the low temperature region, the FC and ZFC curves diverge considerably for all samples, which proves the existence of typical spin glasses, which may also be ascribed to magnetic anisotropy. A spin glass-like state is generally prompted by the coexistence of competing AFM and FM interactions. With a decreasing temperature, a PM–FM phase transition was observed at the Curie temperature. $T_C$ is given at the lowest point of the first derivative of the curve $M(T)$ ($dM/dT$) (inset Fig. 4). The $T_C$ value goes from 354 K for $x = 0.00$ to 301 K for $x = 0.10$. This change has been attributed to the modification of the Mn–O–Mn bond angle. Doping with the slightly larger Ni$^{2+}$ ($r_{Ni}^{2+} = 0.69$ Å) for Mn$^{3+}$ ($r_{Mn}^{3+} = 0.645$ Å) decreases the mean value of the radius of the manganese-site, alters the Mn$^{3+}$/Mn$^{4+}$ ratio and decreases the bond angle $\theta_{(Mn(Ni)-O-(Mn(Ni))}$. In the La0.6–Ba0.2Sr0.2Mn3+Ba0.2Sr0.2Mn3+Ni2+O3 sample, ferromagnetism is confined by the DE interaction between the Mn$^{3+}$ and Mn$^{4+}$ ions. Taking into account the neutrality of the charges (La0.6–Ba0.2Sr0.2Mn3+Ba0.2Sr0.2Mn3+Ni2+O3) of the samples, the substitution of Ni$^{2+}$ transforms the average valence state of Mn$^{3+}$ to Mn$^{4+}$. This weakening of the Mn$^{3+}$ ions essentially induces a reduction in the jumps of the electrons ($e$) and the progressive suppression of the DE interaction subsequently leads to a reduction in ferromagnetism. Moreover, the competition between the AFM and FM interaction exchange is reinforced. On the other hand, when the Ni content increases, $M$ decreases in the FM region and that is consistent with the results in ref. 16 and 42.

The most important cause of the decrease in $T_C$ is the reduction of the one-electron bandwidth $W_d$. It is given as:

$$ W_d = \frac{\cos^2 \left(\frac{\pi}{2} - \theta_{(Mn(Ni)-O-(Mn(Ni))}\right)}{Mn(Ni-O)}^{3.5} $$

Fig. 5 The inverse magnetic susceptibility $\chi^{-1}$ versus temperature. The inset shows the field dependence of the magnetization curves at 10 K.
Fig. 6 Magnetic hysteresis curves at $T = 10$ K for the LBSMNO samples. The inset shows a zoomed in view of the central portion of the hysteresis at a low field.

The increase in the Ni content results in a greater length of the $d_{(\text{Mn(Ni)})-O}$ bond and a reduction in the bond angle $\theta_{(\text{Mn(Ni)})-O-(\text{Mn(Ni)})}$, and therefore a weaker bandwidth $W$ (Table 2) which causes the decrease of $T_C^{14,45}$ In fact, this reduction in $W$ leads to a reduction in the FM coupling between neighboring manganese atoms.

In addition, it is interesting to understand the behavior of $M$ vs. temperature in the FM region. In this context, and according to Lonzarich and Taillefer, magnetobility obeys the theory of spin waves. At low temperatures, this theory is that the magnetization has multiplied in $T^{1/2}$ (Bloch’s law) and over a wide range of temperatures in $T^2$, yet in the vicinity of $T_C$ it varies as follows: $(1 - T^{4/3}/T_C^{4/3})^{1/2}$.

In the FM region, the $M$ data has been adjusted by this relation:

$$M(T) = M_0 + M_{1/2}T^{1/2} + M_2T^2$$

Here $M_0$ is the spontaneous magnetization. Fig. 5 presents the best fit curves. It can be confirmed that the FM behavior of La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ may be owing to spin waves.

For $T > T_C$, the PM region, the Curie-Weiss law was used to analyse the inverse of magnetic susceptibility ($\chi^{-1} = H/M$):

$$\chi = \frac{C}{T - \theta_{CW}}$$

Here, $\frac{C}{3k_B} = \frac{\mu_0^2}{k_B}$ is the Curie constant and $\theta_{CW}$ is the paramagnetic-Curie temperature. These parameters were obtained using the fit of curve $\chi_{M^{-1}}(T)$ (Fig. 5) and its values are also given in Table 3. The positive value of $\theta_{CW}$ suggests that the ferromagnetic interactions between the nearest neighbors are dominant in the system, which could be due to DE Mn$^{3+}$–O$^{2-}$–Mn$^{4+}$ coupling. When $x$ increased, this parameter decreased, which indicates the weakening of the ferromagnetic interactions. The values of $\theta_{CW}$ are higher than those of $T_C$, which indicates the presence of magnetic inhomogeneity above $T_C$.

The experimental effective moment $\mu_{exp}$ can be calculated using the parameter $C$ and the values are given in Table 3.

The theoretical effective paramagnetic moment for La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ compositions could be calculated using the following expression:

$$\mu_{eff}^{theoretical} = \sqrt{(0.6 - x)\mu_{eff}^2(Mn^{3+}) + (0.4 - x + y)\mu_{eff}^2(Mn^{4+}) + \chi_{eff}^2(Ni^{2+})}.$$
The remanence ratio ($R$) is utilized to comprise the isotropic nature of our investigated compounds. The values of remanence varied in the range of $5$–$13$ emu g$^{-1}$. The ratio ($R$) is given by:

$$R = \frac{M_r}{M_s}.$$  

We have summarized the values of $R$ in Table 3. The small obtained values confirm the isotropic natures. In this context, for magnetic recording and memory devices, it is advantageous to have higher remanence ratios. The values of $R$ reveal an increasing trend with Ni$^{2+}$ substitution.

### 3.4 Magnetocaloric properties

We have shown previously that there is a phase transition around $T_C$. Therefore, to calculate the change in magnetic entropy ($-\Delta S_M$), it is necessary to know the order of this transition.

We have presented in Fig. 7(a–c), the external $\mu_0H$ variation of the isothermal magnetization at different temperatures around $T_C$. $M$ increases rapidly at low $\mu_0H$ and then achieves saturation, which shows ferromagnetic behavior. Above $T_C$, thermally unsettled magnetic moments yield to increase magnetizations linearly at high temperatures, which means PM behavior. This phenomena demonstrates the magnetic phase transition.

In the inset of Fig. 7(a–c), we have presented the Arrott plots ($M^2$ vs. $\mu_0H/M$) for the La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ ($0 \leq x \leq 0.1$) compounds, from these curves we can conclude the nature of the magnetic phase transition. The slope of the curves is positive, so the transition is second order, according to Banerjee’s criteria. The MCE is an intrinsic characteristic of magnetic materials. Its principle is based on cooling or heating compounds when subjected to a magnetic field under adiabatic conditions, which is maximized when materials are close to their magnetic control temperature.

$$\Delta S_M(T, \mu_0H) = S_M(T, \mu_0H) - S_M(T, 0)$$

$$= \int_0^{\mu_0H_{max}} \left( \frac{\partial S}{\partial \mu_0H} \right)_T \mu_0 d\mu_0H$$

(8)

$(-\Delta S_M)$ was produced by varying $\mu_0H$ from zero to $\mu_0H$ by exploiting Maxwell’s relation.

Fig. 7  Magnetization versus field ($M$ vs. $\mu_0H$) curves for LBSMNO compounds at 5 K. The inset: $M^2$ vs. $\mu_0H/M$ plots around $T_C$. 

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The peaks of the elaborated samples are the same as those of the experiment in the vicinity of \( T_c \), where\( \mu_0 H = m_0 H \) is the experimental value from the \( M(T) \) curve at \( \mu_0 H \).

We can use the following expression:

\[
\Delta S\left(\frac{T_1 + T_2}{2}\right) = \left(\frac{1}{T_1 - T_2}\right) \left[ \int_{m_0 H_{\text{max}}}^{m_0 H} M(T_2, \mu_0 H) \mu_0 dH - \int_{0}^{m_0 H_{\text{max}}} M(T_1, \mu_0 H) \mu_0 dH \right]
\]

where \( T_1 \) represents the temperatures of hot sinks and \( T_2 \) represents the temperatures of cold sinks.

The predicted \( -\Delta S_M \) vs. temperature plots are shown in Fig. 8 at different \( \mu_0 H \) values. It can be seen that \( -\Delta S_M \) depends on \( \mu_0 H \) and the temperature until a maximum value of \( -\Delta S_M^{\text{max}} \) is reached around \( T_c \). \( -\Delta S_M \) increases with the increase of \( \mu_0 H \) for each compound due to the spin effect, which becomes important with the increase of \( \mu_0 H \). The \( -\Delta S_M^{\text{max}} \) for \( x = 0, 0.05 \) and \( 0.1 \) are 7.65, 5.44, and 4.45 J kg\(^{-1}\) K\(^{-1}\), respectively, at \( \mu_0 H = 5 \) T. Although, when increasing the Ni ratio, \( -\Delta S_M^{\text{max}} \) and \( T_c \) decrease. This can be explicited by the lowering of the Mn\(^{3+}\)/Mn\(^{4+}\) ratio, which goes from 1.5 (\( x = 0 \)) to 0.8 (\( x = 0.1 \)) and subsequently favors the DE interaction of Mn\(^{3+}\)–O–Mn\(^{4+}\) over the superexchange (SE) interaction of Mn\(^{3+}\)–O–Mn\(^{4+}\), Mn\(^{3+}\)–O–Mn\(^{3+}\), and Ni\(^{3+}\)–O–Ni\(^{3+}\). This result is strongly affected by structural parameters, such as decreasing the bond angles (Mn/Ni)–O–(Mn/Ni) and increasing the bond distances (Mn/Ni)–O.

\( -\Delta S_M^{\text{max}} \) is not the only factor that determines the applicability of such a material, but also the temperature range over which it remains considerable is significant.

The relative cooling power (RCP) is another very important parameter along with \( -\delta \), which defines the amount of heat that can be released between cold and hot sinks in an ideal refrigeration cycle and can be given by the following formula:

\[
RCP = -\Delta S_M^{\text{max}} \times \delta_{\text{FWHM}}
\]
Here $\Delta S_{M}^{\text{max}}$ represents the maximum of $\Delta S_M$ and $\delta T_{\text{FWHM}}$ is the full width at half maximum.

Fig. 9 present the relative cooling power as a function of $\mu_0H$ for our compounds. The values of RCP increase with increasing $\mu_0H$ and reach about $214 \text{ J kg}^{-1}$ for $x = 0$, $230 \text{ J kg}^{-1}$ for $x = 0.05$ and $285 \text{ J kg}^{-1}$ for $x = 0.1$ at $\mu_0H = 5 \text{ T}$. To better understand the performance of the MCE of our compounds, the values of $RCP$ increase with increasing curve by normalizing all the materials can be used in the field of magnetic refrigeration.

On the other hand, to affirm the nature of phase transition, Franco et al. proposed a phenomenological universal curve for the field dependence of $\Delta S_{M}$. We can construct the universal curve by normalizing all the $\Delta S_{M}^{\text{max}}$, $\Delta S_{M}(T, \mu_0H)/\Delta S_{M}^{\text{max}}$ below and above $T_C$, by imposing that the position of two additional reference points in the curve correspond to $\theta = \pm 1$.

$$\theta = \begin{cases} 
\frac{T - T_C}{T_1 - T_C}, & T \leq T_C \\
\frac{T - T_C}{T_2 - T_C}, & T \geq T_C 
\end{cases}$$  \hspace{1cm} (11)

Here $T_1$ and $T_2$ are chosen as reference temperatures, such that $\Delta S_{M}(T_1,2) = 1/2\Delta S_{M}^{\text{max}}$.

By referring to Banerjee’s criteria for a 2nd order PM–FM transition, all $\Delta S_{M}$ curves at different $\mu_0H$ values should merge into one curve with temperature scaling. If not, the samples follow a 1st order phase transition. Fig. 10 represents the evolution of $\Delta S_{M}(T, \mu_0H)/\Delta S_{M}^{\text{max}}$ vs. temperature $\theta$ at different $\mu_0H$ values for $x = 0.05$, for example. In this figure, all the data collapse into a single master curve around $T_C$, indicating the 2nd order nature of this phase transition. These results are in good accordance with those obtained by the Banerjee criterion discussed before. In addition, this universal curve can be used for practical purposes, such as extrapolating results to fields or temperatures not available in the laboratory, improving data resolution and deconvoluting the response of overlapping magnetic transitions.

We can adjust this curve by the Lorentzian function:

$$\Delta S = \frac{\alpha}{y + (\theta - \gamma)^2}$$  \hspace{1cm} (12)

Here $\alpha$, $\beta$ and $\gamma$ are adjusted parameters. Given the asymmetry of the curve, two ensembles of different constants must be used:

Table 4 Summary of LBSMNO magnetocaloric values compared to other manganite materials

| Composition                  | $T_C$ | $|\Delta S_{M}^{\text{max}}| (\text{J kg}^{-1} \text{ K}^{-1})$ | RCP (J kg$^{-1}$) | $\mu_0H$ (T) | Ref. |
|------------------------------|-------|---------------------------------------------------------------|-------------------|--------------|------|
| Gd                           | 293   | 5                                                             | 153               | 2            | 46   |
| Gd$_x$(Sr$_{2}$Ge$_2$)       | 275   | 18.5                                                           | 535               | 5            | 47   |
| La$_{0.7}$Sr$_{0.3}$Mn$_{0.95}$Ti$_{0.05}$O$_3$ | 308   | 2.2                                                            | 90                | 2            | 48   |
| La$_{0.7}$Ba$_{0.3}$Sr$_{2}$MnO$_3$ | 354   | 7.65                                                           | 214               | 5            | This work |
| La$_{0.7}$Ba$_{0.3}$Sr$_{2}$Mn$_{0.95}$Ni$_{0.05}$O$_3$ | 320   | 5.44                                                           | 230               | 5            | This work |
| La$_{0.7}$Ba$_{0.3}$Sr$_{2}$Mn$_{0.9}$Ni$_{0.1}$O$_3$ | 301   | 4.45                                                           | 285               | 5            | This work |
| La$_{0.7}$Ba$_{0.3}$Sr$_{2}$Mn$_{0.95}$Fe$_{0.05}$O$_3$ | 354   | 3.88                                                           | 82                | 2            | This work |
| La$_{0.7}$Ba$_{0.3}$Sr$_{2}$Mn$_{0.95}$Co$_{0.05}$O$_3$ | 320   | 2.69                                                           | 98                | 2            | This work |
| La$_{0.7}$Ba$_{0.3}$Sr$_{2}$Mn$_{0.9}$Ni$_{0.1}$O$_3$ | 301   | 2.37                                                           | 121               | 2            | This work |
| La$_{0.6}$Sr$_{0.4}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ | 260   | 1.7                                                            | 83                | 2            | 49   |
| La$_{0.6}$Sr$_{0.4}$Mn$_{0.9}$Co$_{0.1}$O$_3$ | 328   | 5                                                             | —                 | 5            | 50   |
The inset (bottom) corresponds to the conducting region of the experimental values in the metallic region, for $T > T_C$. However, for $x = 0.00$, the value is close to the values of the mean field model. For $x = 0.05$ and 0.1, these values do not coincide with the predicted value of the mean field of 0.66. This difference is probably due to local inhomogeneities around $T_C$.\(^{66}\)

### 3.5 Electrical properties

Fig. 12 presents the variation of electrical resistivity ($\rho$) vs. temperature ($T$) for our samples. All the samples are magnetically ordered and the resistivity exhibits a metallic behavior for low temperatures, resulting from a strong ferromagnetic coupling. Semiconductor behavior (SC) is reported at higher temperatures. It can be concluded that these samples undergo a semiconductor-to-metal (SC-M) transition at $T = T_{M-SC}$. With increasing Ni concentration, this peak temperature $T_{M-SC}$ decreases (Table 5). From this table, one can see that $T_{M-SC}$ for all the doped materials is much lower than $T_C$. From this result, it can be said that the transport properties are governed by the presence of inter-grain boundaries.

To better understand the contribution of the different factors causing the conduction mechanism below the transition temperature ($T < T_{M-SC}$), the $\rho(T)$ curve was fitted using different theoretical models.

Conduction electrons meet different competitors, including scattering of the grain/domain boundary, electron–magnon scattering and electron–electron scattering. Using the following empirical relation,\(^{67}\) the electrical resistivity data is analyzed:

$$\rho_{FM} = \rho_0 + \rho_1 T^2 + \rho_2 T^5$$

Below $T_{C}$, $n$ has been predicted to be 1 and the materials are in the FM state. However, above $T_C$, it is equal to 2 in the PM zone, according to the Curie–Weiss law. Yet, recent experimental data indicates a deviation from $n = 0.66$, in the case of a few soft magnetic amorphous compounds. The temperature dependence of $n$ is shown in Fig. 11. The values of $n$ are found to be 0.67, 0.45 and 0.32 for $x = 0.00$, 0.05 and 0.10, respectively. For $x = 0$, the value is close to the values of the mean field model. However, for $x = 0.05$ and 0.1, these values do not coincide with the predicted value of the mean field of 0.66. This difference is probably due to local inhomogeneities around $T_C$.\(^{66}\)

**Table 5** The best fit parameters gated with the experimental resistivity data utilizing eqn (17)

| $x$ | $\rho_0$ (Ω cm) | $\rho_1 \times 10^{-7}$ (Ω cm K$^{-2}$) | $\rho_2 \times 10^{-15}$ (Ω cm K$^{-4}$) | $A$ (× 10$^{-7}$ Ω cm) | $\delta_0/\delta_0$ (K) | $U_0/\delta_0$ (K) | $\tau_{C_{mod}}$ (K) | $R^2$ |
|-----|-----------------|---------------------------------|---------------------------------|-----------------|-----------------|-----------------|-----------------|---------|
| 0.00 | 0.0011 | 74.39 | 72.73 | 6.47 | 2100 | 8224 | 305 | 0.9998 |
| 0.05 | 0.0015 | 94.60 | 1.28 | 4.65 | 1390 | 7822 | 297 | 0.9995 |
| 0.10 | 0.0022 | 1.13 | 2.32 | 3.45 | 780 | 6993 | 275 | 0.9999 |
Here $\rho_0$ is residual resistivity due to the domain or grain boundaries, $\rho_2 T^2$ is the contribution from the electron–electron scattering process to the electrical resistivity and $\rho_3 T^3$ is associated with the electron–phonon interaction.\textsuperscript{68}

The values of the electrical resistivity were adjusted using eqn (14) and in the inset of Fig. 13, we have given the best fit. In Table 5 we have grouped together the estimated values of the adjusted parameters.

Above ($T > T_{\text{M-SC}}$), the resistivity is simulated by the SPH mechanism.\textsuperscript{69}

\[ \rho = \rho_0 \exp \left( \frac{E_a}{k_B T} \right) \]

where $A$ and $E_a$ are the coefficient of resistivity and activation energy associated to polaron binding energy, respectively. We have fitted the variation of electrical resistivity (see the inset of Fig. 12) and the results are given in Table 5. We calculated the hopping energies $E_a$ and we have deduced that the values of $E_a$ are 180, 86 and 67 meV for $x = 0$, 0.05 and 0.1, respectively.

To understand the transport mechanism of the total resistivity over the whole temperature range, we used a phenomenological percolation model.\textsuperscript{70} For this model, resistivity is defined based on the contributions of the FM clusters in the PM region. Thus, the resistivity is expressed by the following expression:

\[ \rho = \rho_{\text{FM}} f + \rho_{\text{PM}} (1 - f) \]

Here $f$ is the volume fraction of the ferromagnetic phase and $(1 - f)$ is the volume fraction of the paramagnetic phase.

The volume fraction follows the Boltzmann distribution and this is expressed via the following equation:

\[ \rho = \rho_0 \exp \left( \frac{\Delta U}{k_B T} \right) \]

where $\Delta U = -U_0 (1 - T/T_{\text{C}}^{\text{mod}})$ is the energy gap between the FM and PM states. $T_{\text{C}}^{\text{mod}}$ is the temperature of resistivity maxima and $U_0$ is taken as the energy gap for temperatures lower than $T_{\text{C}}^{\text{mod}}$.

With $T = T_{\text{C}}^{\text{mod}}, f = f_c = 0.5$ where $f_c$ is called a percolation threshold.\textsuperscript{71} Where $f < f_c$, the sample remains semiconducting and for $f > f_c$ it acquires a metallic phase.\textsuperscript{72}

Hence, in the entire temperature range eqn (16), can be given as:

\[ \rho = \rho_0 + \rho_2 T^2 + \rho_3 T^3 + AT \exp \left( \frac{E_a}{k_B T} \right) (1 - f) \]

The data evaluated from eqn (17) are in agreement with the experimental results. It can be seen that the percolation model adequately describes the resistivity behavior over a wide range of temperatures, including the phase transition region. We have grouped the most suitable parameters in Table 5 and in Fig. 13, we have presented the fit of the data.

The inset in Fig. 13 shows $f(T)$ vs. temperature for all samples. Below $T_{\text{M-SC}}$, the volume concentration of the ferromagnetic phase remains equal to 1. This proves the strong dominance of the FM part in this zone. Afterwards, $f(T)$ starts to lower to zero, since the metallic state (FM) moves to a semiconductor state (PM). This result proves the validity of the percolation approach.

4. Conclusion

We have investigated the physical properties of polycrystalline La$_{0.6}$Ba$_{0.2}$Sr$_{0.2}$Mn$_{1-x}$Ni$_x$O$_3$ samples. Their crystal structures correspond to a rhombohedral structure, with the $R3\bar{c}$ space group without any secondary phase. When the substitution rate increases, the unit cell volume decreases. The magnetic and electrical measurement data indicate that our compounds show FMM behaviour at low temperature ($T < T_{\text{M-SC}}$) and PMS behaviour above $T_{\text{M-SC}}$. This temperature decreases as the Ni substitution increases, due to the bandwidth reduction. The values of $(-\Delta U_{\text{mod}})$ at $\mu\phi H = 5$ T are 7.40 J kg$^{-1}$ K$^{-1}$, 5.6 J kg$^{-1}$ K$^{-1}$ and 4.48 J kg$^{-1}$ K$^{-1}$ for $x = 0.00, 0.05$ and 0.10, respectively. The magnetocaloric performance of these samples indicates that the polycrystalline La$_{0.6}$Ca$_{0.1}$Sr$_{0.3}$Mn$_{1-x}$Ni$_x$O$_3$ compounds are good candidates for magnetic refrigeration at room temperature.

Conflicts of interest

There are no conflicts to declare.

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