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**Magnetic and magnetocaloric properties in $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$
($x=0.11$ and 0.133) perovskite manganites**

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Abstract:

A systematic investigation of structural, magnetic and magnetocaloric properties for $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) manganites is reported. X-ray powder diffraction (XRD) patterns suggest that our samples crystallize in the orthorhombic perovskite structure with a $Pbnm$ space group. Magnetization temperature dependence under the field-cooled cooling (FCc), field-cooled warming (FCw) and zero-field-cooling (ZFC) modes exhibit a ferromagnetic(FM)- paramagnetic(PM) phase transition at T_C temperature increasing from 120K for $x=0.11$ to 145K for $x=0.133$. An analysis using the Banerjee's criterion curves near T_C indicates that $x=0.11$ displays a second-order transition while $x=0.133$ displays a first order magnetic phase transition. The analysis is further confirmed by the phenomenological universal curves of the normalized entropy variation as a function of rescaled temperature. The maximum-magnetic entropy change ($-\Delta S_M^{max}$) and relative cooling power (RCP) were estimated to 1.68 J /kg K and 89.45 J /kg for $x=0.11$ and 4.11 J/ kg K and 132.45 J /kg for $x=0.133$ under 3T, respectively. The experimental approach mixing three different alkaline earth on the A-site perovskite significantly improves the broadening of the magnetic entropy change temperature dependence and then the relative cooling refrigerant capacity. Such approach can be transferred to manganite showing ferromagnetic to paramagnetic phase transition near room temperature for magnetic refrigeration application.

Keywords: Perovskite, Magnetization, Phase transition, Magnetic refrigeration, Modeling and simulation.

1. Introduction

Perovskite type manganite with a general formula $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$, (Ln = rare earth element and A = divalent alkaline earth elements) have gained tremendous attention in the scientific community owing to their several fascinating physical properties such as colossal magnetoresistance (CMR), charge and / or orbital ordering state and large magnetocaloric effect (MCE) [1-5]. Therefore, researchers are interested in these materials because of their exceedingly technological applications like magnetic refrigeration, magnetic field sensors, computer memory systems, etc.

Magnetic refrigeration (MR) systems based on the magnetocaloric effect (MCE) in magnetic materials is an auspicious refrigeration technology thanks to its many advantages over conventional gas compression (CGC) and expansion technique such as high or potential energy efficient, environmental friendliness, economic and ecological cleanliness [6-7].

The MCE is an intrinsic property, and results from the strong coupling of magnetic sub-lattices with a magnetic field. It is simply defined as the adiabatic temperature change (ΔT_{ad}) and/or an isothermal change in magnetic entropy ($-\Delta S_{\text{M}}$) of a system due to a varying magnetic field. Generally, direct MCE comes into a play in the proximity of a magnetic phase transitions at the Curie temperature [5].

There are many materials for magnetic refrigeration application near room temperature.

Gadolinium (Gd) is one of them, it has been considered as the most active material in the magnetic refrigeration technology because it has a large magnetic entropy change $\Delta S_{\text{M}}=10.2\text{J/KgK}$ at $T=294\text{K}$ at 5T. However, the expensive price (4000 \$/kg), easy oxidation and hard preparation of this rare earth prevents it from practical application [8-9]. For this reason, it was necessary to find other cheap and safe alternatives with the same efficiency.

Recent studies have revealed that manganites with perovskite structure are attractive candidates for magnetic refrigerant technology owing to their large MCE close to their Curie temperature. The advantages of manganites are their lower cost, simple production, easily tunable transition temperature, extraordinary chemical stability [10] and high electrical resistivity, which are beneficial for reducing eddy-current heating [11]. Temperature span as large 5K has even been reported around room temperature for manganites showing different chemical composition [12-13].

The parent LaMnO_3 , as a typical compound, is an antiferromagnetic (AFM) insulator. Its antiferromagnetic behavior is characterized via a super-exchange (SE) interaction between Mn^{3+} sites. Partial Substitution of the trivalent rare earth ions (such as La^{3+} , Nd^{3+} , Pr^{3+} etc.) by divalent alkaline earth ions causes the mixed valence states of Mn (Mn^{3+} and Mn^{4+}) and can lead a transition from paramagnetic to ferromagnetic and insulator to metal states .

The magnetic properties of these substituted manganites are mostly explained on the basis of double exchange (DE) interactions between Mn^{3+} and Mn^{4+} ions in the Mn-O-Mn network and Jahn- Teller distortion [14-15].

In this work, the structural, magnetic and magnetocaloric properties of $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) perovskite manganites are reported keeping in mind that mixing three different alkaline earth on the A-site perovskite improve the broadening of the temperature dependence of the maximum magnetic entropy change and then the relative cooling refrigerant capacity [16].

2. Experimental

The perovskite manganites $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) were prepared through the conventional solid-state reaction route using high-purity Nd_2O_3 , CaCO_3 , BaCO_3 , SrCO_3 and MnO_2 powders. Homogeneous stoichiometric mixtures were heated in air at 900°C for 48 hours for decarbonatation. Then these were pelletized at 1100°C for 24 hours. Finally, powders were reground, pressed into pellets form and then sintered at 1400°C during 24 h in air to assure homogenization. The morphology and composition were investigated by Scanning Electron Microscopy (SEM) equipped with Energy Dispersive X-ray spectroscopy (EDX) at room temperature. The phase purity and crystallographic structure of the materials were determined by XRD patterns with $\text{CuK}\alpha$ radiation (1.5406 \AA) in the $18^\circ \leq 2\theta \leq 81^\circ$ range with a step width of 0.02° and a count time of 18s/step. The diffraction patterns were carried out by the Rietveld refinement process using program FULLPROF software [17]. The magnetization measurement as a function of temperature (field-cooled cooling (FCc), field-cooled warming (FCw) and zero- field cooling) were reported in the range 5–350 K under 0.02T using a superconductive quantum interference device. The isothermal magnetic entropy change of the material were calculated from $M(H)$ isotherms up to 3T at various temperatures in steps of 5 K.

3. Results and discussions

3.1. Microstructure and structural analysis

The chemical composition were investigated by Energy Dispersive X-ray spectroscopy (EDX) technique. Fig. 1a-b show the EDX spectra for the $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) samples. These spectra show peaks corresponding to the elements of Nd, Sr, Ba, Ca, and Mn. The estimated atomic percentages are shown in the inset of Fig.1. It is a semi quantitative analysis and the given atomic % are consistent with the targeted chemical composition mixing the same content of Ca, Sr and Ba.

The shape and grain size of the powder samples $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) were studied by Scanning Electron Microscopy (SEM) as presented in Fig. 1. The grain size was estimated from the SEM micrographs by considering as many particles as possible. The first observation shows that both samples are homogenous with average grains size ranging from 1.44 to $1.53 \mu\text{m}$ for $x=0.11$ and 0.133 , respectively.

Structural analysis of the $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) samples was carried out by powder X-ray diffraction. Fig.2(a) displays the XRD patterns collected for $x=0.11$ compound at room temperature whereas the one's for $x=0.133$ is shown in supplementary Information Figure 2(b)). In spite of the very small peaks associated with the phases of non-magnetic secondary alkaline earth metal carbonates (principal peak around $2\theta=31^\circ$) because of CO_2 adsorption, the main phase is single for $x=0.11$. For $x=0.133$, traces of $(\text{Ca,Sr,Ba})_2\text{Mn}_2\text{O}_5$ (at $2\theta=25.6^\circ$ and 32.3°) are found in the XRD pattern with the main peak corresponding to unknown phase despite the synthesis under air.

The XRD data was analyzed by using the Rietveld method with the Fullprof program [17]. The structure is indexed in the orthorhombic structure with a space group $Pbnm$. The quality of the Rietveld refinement is assessed via the goodness of the fit factor χ^2 . The detailed results pertaining to the refinement are gathered in Table 1.

As expected, the lattice parameters as well as the unit cell volume increase with x . This is associated with the larger ion radii of the alkaline earth replacing Nd^{3+} at the A-site of the perovskite structure.

As first assumption, the distortion of the crystal structure is governed with Goldschmidt tolerance factor (t_G) [18] defined by:

$$t_G = \frac{\langle r_A \rangle + \langle r_O \rangle}{\sqrt{2(\langle r_B \rangle + \langle r_O \rangle)}} \quad (1)$$

Here, $\langle r_A \rangle$, $\langle r_B \rangle$ and $\langle r_O \rangle$ represent the average ionic radius of the A and B cations and oxygen anion, respectively which values are given by Shannon [19]. If t_G is equal to unity [20], the lattice structure is defined as ideal cubic perovskite but any deviation from this value upward and downward is the signature of a distorted perovskite structure. In the region $t_G < 0.96$, an orthorhombic symmetry is suggested for the compounds, while for $0.96 < t_G < 1$ is a rhombohedral one's that is expected. The t_G values for the present samples are mentioned in Table 1. The calculated tolerance factor t_G of our samples are consistent with the XRD patterns and the resulting orthorhombic structure.

3.2. Magnetic properties

Fig.3 represents temperature dependencies of magnetization in three various modes zero-field-cooled (Z_{FC}), field cooled cooling (FC_c) and field cooled warming (FC_w) for $Nd_{1-3x}Ba_xCa_xSr_xMnO_3$ ($x=0.11$ and 0.133) compounds measured under 200Oe. Starting at 350K, our samples clearly show a paramagnetic (PM) to ferromagnetic (FM) transition when temperature decreases. Both M-T data plotted in Fig.3 (a-b) showed nearly identical features, the M_{FC} (M_{FC_w} and M_{FC_c}) and M_{ZFC} curves coincide in the paramagnetic phase above 150K. However as the temperature is reduced further, the curves do not overlap and start splitting and subsequently a sharp rise in both M_{FC} and M_{ZFC} is seen with decrease in temperature, which may be attributed to the existence of magnetic domain nucleation in the compounds [16].

Transition temperatures (T_C) can be deduced accurately from the minimum of the first derivative magnetization curves (dM/dT) for the ZFC curve versus temperature. They are shown as inset in Fig.3(a-b) and their values are listed in Table 2. T_C slightly increases with x in $Nd_{1-3x}Ba_xCa_xSr_xMnO_3$, which may be related to the increase of $\langle r_A \rangle$ and/or t_G as mentioned in the Table1. Furthermore, for a constant Mn^{3+}/Mn^{4+} ratio, a quite large Ca, Sr and Ba cation size mismatch effect [21] on the magnetic properties is also suggested when the Curie temperature for our sample ($x= 0.133$) equal to 145K is compared to the 273 K reported for $Nd_{0.6}Sr_{0.4}MnO_3$ compounds [22].

Plots of $1/\chi$ (T) for $x=0.11$ and 0.133 compounds, are presented in the inset of Fig. 3a–b. They obey the Curie-Weiss (CW) law [23]:

$$\chi(T) = \frac{C}{(T - \theta_{CW})} \quad (2),$$

in the PM region ($T > T_C$), θ_{CW} is the Curie-Weiss temperature representing the molecular mean field between the magnetic moments and C is the Curie constant defined as:

$$C = \frac{N_A \mu_B^2}{3k_B} \mu_{eff}^2 \quad (3)$$

where $k_B = 1.38016 \times 10^{-16}$ ergK⁻¹ is Boltzmann constant, $N_A = 6.023 \times 10^{23}$ mol⁻¹ is Avogadro number, $\mu_B = 9.274 \times 10^{-21}$ emu is Bohr magneton and μ_{eff}^{exp} the effective moment expressed in Bohr magneton.

The Curie constant C and θ_{CW} can be determined from a linear fit to paramagnetic phase of χ^{-1} (T) under ZFC modes. However, our inverse magnetic susceptibility can only be fitted for small temperature segments whose experimental paramagnetic moments μ_{eff}^{exp} continuously increase. Two arbitrary temperature ranges were chosen to illustrate that phenomenon. As seen in table 2, the positive values of θ_{CW} , higher than T_C indicate the presence of short range ferromagnetic interactions between the neighboring atomic spins. It illustrates magnetic inhomogeneity above T_C .

Furthermore, based on the obtained C value, the experimental paramagnetic moments μ_{eff}^{exp} (in unit of Bohr magneton μ_B) can be determined with the following equation:

$$\mu_{eff}^{exp} = \sqrt{\frac{3k_B C}{N_A}} = \sqrt{8C} \mu_B \quad (4)$$

and compared with, the theoretical effective moment μ_{cal} of $Nd_{1-3x}Ba_xCa_xSr_xMnO_3$ ($x=0.11$ and 0.133) calculated by the relation:

$$\mu_{eff}^{theo} = \sqrt{(1 - 3x)[\mu_{Nd^{3+}}^2 + \mu_{Mn^{3+}}^2] + 3x\mu_{Mn^{4+}}^2} \quad (5)$$

The theoretical values for the ionic magnetic moments in the spin only hypothesis for the manganese ions are $\mu_{eff}(Nd^{3+}) = 3.62 \mu_B$, $\mu_{eff}(Mn^{3+}) = 4.9 \mu_B$ and $\mu_{eff}(Mn^{4+}) = 3.8 \mu_B$.

The μ_{eff}^{exp} and μ_{eff}^{theo} values are listed in Table 2. Interestingly, our paramagnetic moments are on the same range as those already reported in $La_{0.7}Ca_{0.3}MnO_3$ sample [24] or $Nd_{0.6}Sr_{0.4}MnO_3$ [23]. Our analysis of the data collected up to 350K do not allow us to extract a μ_{eff}^{exp} close to the ionic theoretical one's suggesting the Mn^{3+} -

Mn^{4+} spin clusters already at such temperature. Finally, the deviation seen in our inverse susceptibility for sample $x=0.133$ around 320K may likely due to the traces of $(Ca,Sr,Ba)_2Mn_2O_{5+d}$ even if air atmosphere was used during the synthesis process. However, the paramagnetic behavior observed above 320K still deviate from the ionic one's.

3.3.Magneto-caloric effect

To investigate the MCE properties, magnetization isotherms were measured around T_C at temperature intervals of 5K. Fig.4 shows the magnetization isotherms (M-H) of the samples $Nd_{1-3x}Ba_xCa_xSr_xMnO_3$ ($x=0.11$ and 0.133) around T_C in the 0-3T magnetic field range. Below Curie temperature, the (M-H) curves of both samples rises rapidly at low magnetic fields and afterwards tended to saturate at high fields, which confirms the ferromagnetic behavior. Interestingly, if the magnetization saturation found for $x= 0.133$ is in the range of those already reported for $Nd_{0.6}Sr_{0.4}MnO_3$ [25], the S-shape near the Curie temperature has never been reported yet. Above T_C , M-H curves for $x=0.11$ exhibits an almost linear behavior, which is typical for paramagnetic materials.

For deeper understanding the type of the magnetic phase transition for the $Nd_{1-3x}Ba_xCa_xSr_xMnO_3$ ($x=0.11$ and 0.133) compounds, the Arrot plots H/M versus M^2 based on the M-H data are constructed (Fig. 5).

According to the Banerjee's criterion [26], the nature of magnetic transition can be determined from the slope of the straight line in the Arrott plots ($H/M-M^2$), a negative or positive slope of these plots respectively implies a first-order or second-order transition.

For compounds under investigation, it can be seen Fig.5(a) for $x=0.11$, that all the Arrot curves H/M versus M^2 clearly exhibit positive slope in a wide temperature range revealing that this transition is a second order phase transition (SOPT). However, as seen in Fig.5(b) for $x=0.133$ sample, the slopes of some H/M vs M^2 plots at high temperatures (above T_C) are negative, the magnetic transition is then first order (FOPT). The first order nature of the transition is further supported by the narrowing of the first derivative magnetization curve (dM/dT) versus temperature in comparison with the other sample as shown in insets in Fig.3(a-b). Similar behavior have already been reported in other manganites [28,29].

The isothermal magnetic entropy change, (ΔS_M), is an important parameter to characterize the (MCE). From the magnetization isotherms $M(H, T)$ reported in Fig 4, we can estimate the MCE from the entropy change.

On the basis of the thermodynamic theory, the isothermal-field induced magnetic entropy change (ΔS_M) from 0 to H_{max} can be calculated through the formula [30]:

$$\Delta S_M(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^{H_{max}} \left(\frac{\partial S}{\partial T} \right)_H dH \quad (6)$$

The relationship between entropy and magnetization can be obtained using the following Maxwell equation:

$$\left(\frac{\partial M}{\partial T} \right)_H = \left(\frac{\partial S}{\partial H} \right)_T \quad (7)$$

From Eq (7) and (8) one can get:

$$\Delta S_M \left(\frac{T_1 + T_2}{2} \right) = \frac{1}{T_1 - T_2} \left[\int_0^{H_{max}} M(T_2, H) dH - \int_0^{H_{max}} M(T_1, H) dH \right] \quad (8)$$

where H_{max} is the maximum external field.

Fig. 6 shows the temperature dependence of magnetic entropy change ($-\Delta S_M$) calculated under different applied magnetic fields change from 1 to 3T for $Nd_{1-3x}Ba_xCa_xSr_xMnO_3$ ($x=0.11$ and 0.133) samples. These two compounds show similar behavior, i.e. the ($-\Delta S_M$) value reaches a maximum $-\Delta S_M^{max}$ near the transition temperature (T_C) at low applied fields and it increases with increasing H which may be due to the improvement of FM interactions. Also as the alkaline earth content increases, maximum entropy change $-\Delta S_M^{max}$ increase (see Table 3). The calculated values of $-\Delta S_M^{max}$ are given in Table 3 and plotted as a function of H (see Fig 7). It is easy to see that $-\Delta S_M^{max}$ is likely proportional to magnetic field.

For $H=3$ T, the maximum values of ($-\Delta S_M$) are found to vary between 1.68 and 4.1 J/kg K for $x=0.11$ and 0.133 , respectively, A comparison of our extracted values with others reported for neodymium bases perovskites manganites, are shown in Table 3.

In general, the large magnetic entropy change in manganites mainly originate from the double exchange interaction between Mn^{3+} and Mn^{4+} ions [31]. Furthermore, the spin-lattice coupling in the magnetic ordering process also plays an important role [32].

Due to strong coupling between spin and lattice, significant lattice change accompanying the magnetic transition in perovskite manganites has been observed [33]. Consequently, the abrupt change in magnetization near T_C for the $x=0.133$

compound would be due to a more significant change of the electron/phonon coupling at the phase transition with respect to the one's for the $x=0.11$ compounds[34]. It would resulting in the larger magnetic entropy change as seen in $\text{La}_{2/3}(\text{Ca}_{1-x}\text{Sr}_x)_{1/3}\text{MnO}_3$ [35].

The relative cooling power (RCP) is related to the refrigeration efficiency of a magnetocaloric material. It is estimated using the following equation:

$$RCP = -\Delta S_M^{max} \times \delta T_{FWHM} \quad (9)$$

where δT_{FWHM} is the full width at half maximum of the ΔS_M peak assuming a gaussian shape.

Fig.8 shows an almost linear behavior of the RCP data of both compounds ($x=0.11$ and 0.133) with respect to the applied magnetic field. This indicates that RCP is powerful field dependent. The obtained values of $-\Delta S_M^{max}$, T_C and RCP at 3T magnetic field for $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) are summarized in Table 3 allowing a simple comparison with other reported neodymium based perovskite manganites. Mixing different alkaline earth on the A-site perovskite improves the broadening of the temperature dependence of the maximum magnetic entropy change and then the relative cooling refrigerant capacity. Such broadening due to Curie temperature distribution has already be pointed out in relation with microstructure change controlled in purpose in the intermetallic $\text{Pr}_2\text{Fe}_{17}$ [36]. However, in our compounds, it is most likely the alkaline earth statistic distribution on the perovskite A-site at the origin of the Curie temperature distribution.

To deeply understand the origin of the MCE near the transition temperature, we have modeled MCE's experimental data in the frame of Landau theory taking into account magnetoelastic couplings and electronic interactions. The Gibbs free energy of the system can be written as:

$$G(M, T) = G_0 + \frac{A(T)}{2} M^2 + \frac{B(T)}{4} M^4 - MH \quad (10)$$

A and B are the temperature dependent of Landau coefficients. For energy minimization ($\frac{\partial G}{\partial M} = 0$), the magnetic equation of state is transformed as:

$$\frac{H}{M} = A(T) + B(T)M^2 \quad (11)$$

Landau's coefficients A and B were determined from the linear fitting region of the Arrot plots (Fig.5).

The corresponding magnetic entropy change (ΔS_M) is determined from differentiation of the magnetic part of the free energy:

$$\Delta S_M(T, H) = -\frac{1}{2}A'(T)M^2 - \frac{1}{4}B'(T)M^4 \quad (12)$$

where $A'(T)$ and $B'(T)$ are the temperature derivatives of the Landau coefficients.

Fig. 9 shows Landau magnetic entropy change ($-\Delta S_M$) at $H=3T$ in comparison with the experimental results. We find a good agreement between the two approaches based on the Maxwell relation (dots) and Landau relation (lines). This agreement further support the impact of the magnetoelastic couplings and electron interactions on the magnetocaloric properties of the $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) compounds.

Finally, Franco and co-workers [39-40] have suggested the phenomenological universal curve for the temperature dependence $\Delta S_M(T)$ as more effective criterion to discriminate the order of phase transition than the Banerjee's one's.

The universal curve is estimated by normalizing all ($-\Delta S_M$) curves with respect to their maxima, $\Delta S^i = \Delta S_M / \Delta S_M^{max}$; and by rescaling the temperature axis by defining another variable θ as following:

$$\theta = \begin{cases} -(T - T_C)/(T_{r1} - T_C); T \leq T_C \\ (T - T_C)/(T_{r2} - T_C); T > T_C \end{cases} \quad (13)$$

where T_{r1} (below T_C) and T_{r2} (above T_C) present the temperature of the reference points that coincide with $\Delta S_M^{max}/2$.

Fig. 10 depicts the dependence of the entropy change ΔS^i versus θ for the two studied compounds measured at different applied fields. As shown in Fig. 10(a) all the experimental points collapse on to one universal curve in the all temperature interval indicating the validity of using the universal curve for $x=0.11$ with successive second order phase transition (SOPT). But, for $x=0.133$ sample (Fig.10 (b)), curves do not collapse onto a single one's and their divergence suggest the occurrence of a first order phase transition (FOPT), which is consistent with the Arrott plots and the sharp magnetization first derivative.

4. Summary

In summary, the structural, magnetic and magnetocaloric properties of $\text{Nd}_{1-3x}\text{Ba}_x\text{Ca}_x\text{Sr}_x\text{MnO}_3$ ($x=0.11$ and 0.133) manganites synthesized via a standard solid state reaction route are investigated. XRD analysis indicate that these samples crystallize in an orthorhombic symmetry with $Pbnm$ space group. A sharper sharp FM-PM phase transition is observed for $x=0.133$ sample. The two samples show large MCE at temperature around 150K. The maximum values of $-\Delta S_M^{\max}$ are 1.68 J/kg K and 4.1J/kg K for $x=0.11$ and $x=0.133$, respectively under 3T. Moreover high values of RCP=89.31 J/kg and RCP=132.19 J/Kg for $x=0.11$ and 0.133 , respectively at $H=3\text{T}$ are shown. These experimental values of magnetic entropy change are in accordance with the Landau theory approach supporting a magnetoelastic coupling at the origin of the observed magnetocaloric effect. For $x=0.11$ composition, the positive slopes in the Arrott plot revealed a second order phase transition (SOPT) which was successfully confirmed by the phenomenological universal curve. While the $x = 0.133$ sample has first order phase transition (FOPT) as expected by the sharp magnetic transition, the magnetization S-shape around the Curie temperature and the jump in the magnetocaloric effect going from $x= 0.11$ to 0.133 .

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