



Effect of A-site ionic disorder on magnetocaloric properties in large band width manganite systems

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ABSTRACT

In this work, we explore the influence of A-site ionic disorder (σ^2) on magnetocaloric properties in relatively larger bandwidth manganite systems like, well known $La_{0.7}Sr_{0.3}MnO_3$ compound. For the study, three isoelectronic manganites with same A-site ionic radius ($\langle r_A \rangle = 1.24\text{\AA}$) i.e. $La_{0.7}Sr_{0.3}MnO_3$ ($\sigma^2 = 1.85 \times 10^{-3}$), $Pr_{0.7}Sr_{0.14}Ba_{0.16}MnO_3$ ($\sigma^2 = 1.17 \times 10^{-2}$) and $Nd_{0.7}Sr_{0.07}Ba_{0.23}MnO_3$ ($\sigma^2 = 1.66 \times 10^{-2}$) samples have been prepared. Magnetic measurements reveal that, upon increasing σ^2 from 1.85×10^{-3} to 1.66×10^{-2} , ferromagnetic double exchange interaction diminishes and as a result, ferromagnetic ordering temperature (T_C) decreases from 360 K to 100 K. Accordingly, the magnetic entropy change ($-\Delta S_M$) has also been found to decrease from 4.6 J/kg-K to 4.1 J/kg-K on the application of 70 kOe magnetic field. However, for $\sigma^2 = 1.66 \times 10^{-2}$, the value of $-\Delta S_M = 5.7\text{ J/kg}$ is relatively larger compared to the other two values of $-\Delta S_M$. Additionally, increased σ^2 (1.85×10^{-3} to 1.66×10^{-2}) broadens the peak of $-\Delta S_M$ which results in the increase in relative cooling power (RCP) from 80 J/kg to 121 J/kg on application of 20 kOe magnetic field. Critical analysis has been performed to explain the enhancement in RCP with σ^2 and the anomaly in $-\Delta S_M$ for $Pr_{0.7}Sr_{0.14}Ba_{0.16}MnO_3$ ($\sigma^2 = 1.17 \times 10^{-2}$) compound.

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1. Introduction

The magnetocaloric effect (MCE) has recently drawn several attentions due to the possible application in magnetic refrigeration technique which is energy efficient as well as environment-friendly and can be the alternative of the conventional gas-compressor based refrigeration [1–9]. The MCE is defined as the isothermal entropy change due to the application of external magnetic field i.e. $\Delta S_M (= S_M(T, H) - S_M(T, 0))$ under adiabatic condition. Generally, MCE is obtained in the proximity of a magnetic phase transitions [10–13]. Together with the isothermal magnetic entropy change (ΔS_M), another important parameter for magnetic refrigerants is the relative cooling power (RCP). In an ideal refrigeration cycle, the amount of heat transfer between hot and cold end is determined by RCP and it is defined as the twice the area under the ΔS_M versus T curve. The strategy to enhance the RCP is either by getting large ΔS_M or by enhancing the span of ΔS_M over a wide temperature range. Recently, an increasing attention has been paid to look for magnetic refrigerants with large RCP [14–17].

Among the different magnetic refrigerants, the doped perovskite manganites have attracted increasing attentions because of several advantages such as relatively large magnetic entropy change [18,19], tunable T_C [22], chemical stability, low production cost and relatively large resistivity [20] which favors the reduction of loss due to the eddy current heating [21]. The physical properties of doped perovskite manganites with the general formulae $R_{1-x}A_xMnO_3$ (R = rare earth ion, A = divalent ion) are governed by the three factors [23]: the hole doping level x, average A-site ionic radius ($\langle r_A \rangle$) and its disorder. For manganites, electronic bandwidth is directly proportional to the A-site ionic radius ($\langle r_A \rangle$) [24,25] as with the increase of $\langle r_A \rangle$, Mn–O–Mn bond angle increases which favors the electronic conduction. On the other hand, A-site disorder is quantified by the variance of the A-site ionic distribution [26] $\sigma^2 = \sum y_i r_i^2 - \langle r_i \rangle^2$, where $\langle r_i \rangle$ is the average A-site ionic radius, y_i is the fractional occupancies of the i^{th} ion in A-site. The materials with higher electronic bandwidth usually show higher curie temperature [27,28]. Hwang et al. [28] has described that at 30% hole doping, with decreasing $\langle r_A \rangle$ from 1.24 Å to 1.18 Å the PM to FM transition temperature (T_C) decreases from 360 K to 50 K and below $\langle r_A \rangle = 1.18\text{\AA}$ system converts from ferromagnetic to spin glass state. Again, systems showing ferromagnetic transition are usually

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metallic. Thus, from eddy current point of view ferromagnetic system is not suitable for the refrigerant material. On the other hand, enhanced A-site disorder converts the FM metallic systems into the cluster glass state which is insulating in nature [29,30]. Disorder also increase the distribution of the ferromagnetic double exchange interactions strength which results in the broadening in T_C [29]. Therefore, to have a refrigerant near room temperature with reduced eddy current loss and large RCP, one needs a system with large electronic bandwidth (near 1.24Å) together with the quenched disorder to make the system insulating. Though the study on MCE in manganites have been reported earlier [1–9] but to the best of our knowledge, the effect of σ^2 on large bandwidth manganites system has been rarely addressed.

Among the different magnetic materials, one of the most well-known manganites with relatively large electronic bandwidth is $La_{0.7}Sr_{0.3}MnO_3$ [31,32] with PM to FM ordering temperature at 360 K. To study the effect of A-site disorder on MCE for large bandwidth manganite system, we have chosen $\langle r_A \rangle = 1.24\text{\AA}$ of $La_{0.7}Sr_{0.3}MnO_3$ to be fixed and prepared other samples with the same $\langle r_A \rangle$ but with different σ^2 . In this regard, we have prepared $Pr_{0.7}Sr_{0.14}Ba_{0.16}MnO_3$ and $Nd_{0.7}Sr_{0.07}Ba_{0.23}MnO_3$ compounds with $\sigma^2 = 1.85 \times 10^{-3}$ and 1.17×10^{-2} respectively. The detailed MCE study of the compounds has been addressed here. The study shows the enhancement of RCP with increasing σ^2 . The origin of this enhancement has been explained from critical analysis of the compounds.

2. Sample preparation and characterization

The bulk polycrystalline manganites samples with compositional formulae $Ln_{0.7}D_{0.3}MnO_3$ (where Ln = La, Pr, Nd and D = Sr, Ba) has been prepared by the polymeric precursor sol gel method, also known as Pechini method. As a first step, the corresponding amounts of La_2O_3 (or Pr_6O_{11} or Nd_2O_3), MnO_2 and $SrCO_3$ (or $BaCO_3$ or both) of purity 99.9% has been dissolved separately in nitric acid and mixed together in citric acid to convert in citrates. The p^H of the solutions has been adjusted between 6.5 – 7. After getting a sol on slowly evaporating the citrate solution at 80 – 90°C, an equal amount of ethylene glycol has been added as a promoter of citrate polymerization and heated on a hot plate at 180°C to form gel and subsequently has been heated at 250°C until a black porous powder is formed as a complete removal of water molecules. Finally, the decomposed gels has been pelletized and sintered in air 1300°C for 36 h to make bulk samples.

The phase purity of the samples has been checked from x-ray diffraction patterns, recorded at room temperature using Rigaku-TTRAX-III with 9 kW rotating anode Cu-source of wavelength $\lambda = 1.54\text{\AA}$. The magnetic measurements has been performed over the temperature region 5–380 K at applied magnetic fields up to 70 kOe by employing VSM-SQUID (Quantum design).

3. Experimental results and discussion

The room temperature x-ray diffraction pattern of the samples has been shown in Fig. 1. The crystal structure determination has been performed from Rietveld analysis using FULLPROF software which indicates the rhombohedral structure of the $La_{0.7}Sr_{0.3}MnO_3$ sample with $R\bar{3}C$ space group symmetry whereas $Pr_{0.7}Sr_{0.14}Ba_{0.16}MnO_3$ and $Nd_{0.7}Sr_{0.07}Ba_{0.23}MnO_3$ possesses orthorhombic ($Pbnm$) structure. The relatively larger intensity peaks has also been indexed with the corresponding lattice planes in the figures. The extracted lattice parameters with calculated average A-

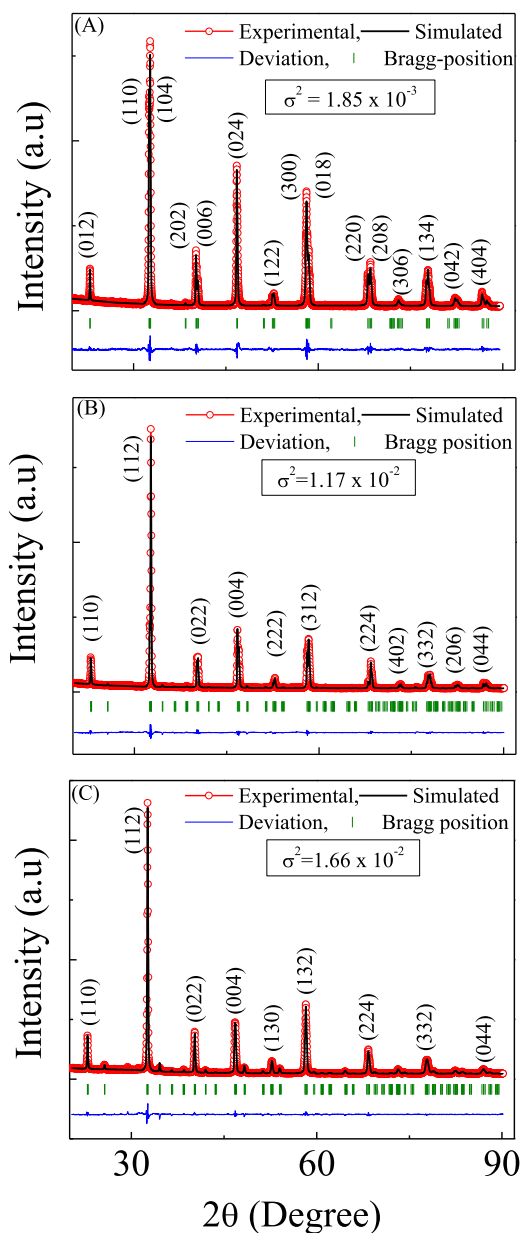


Fig. 1. Room temperature XRD data with its profile fitted data for the samples with A-site ionic disorder (A) 1.85×10^{-3} (B) 1.17×10^{-2} and (C) 1.66×10^{-2} respectively.

site ionic radius $\langle r_A \rangle$ and A-site ionic distribution (σ^2) has been presented in Table 1.

With increasing σ^2 for a fixed ionic radii (1.244), the crystal structure evolves from $R\bar{3}C$ to $Pbnm$. Although, the same structural evolution has also been observed on reduction of ionic radii from 1.244 for $La_{0.7}Sr_{0.3}MnO_3$ to 1.218 in $La_{0.7}Sr_{0.1}Ca_{0.2}MnO_3$ as reported by Phan et al. [33]. Thus superstructure type depends upon both $\langle r_A \rangle$ and (σ^2) [34].

Manganites being strongly correlated in nature, the effect of this A-site variance will also be reflected in magnetic properties. To elucidate the effect of this A-site variance, magnetization measurements as a function of temperature $[M(T)]$ in presence 100 Oe external magnetic field has been performed in all the samples in zero field cooled warming (ZFCW) and field cooled warming (FCW) protocols (Fig. 2).

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