Finite-size effects on the evolution of magnetic correlations and magnetocaloric properties of \( \text{Pr}_{0.4}\text{Bi}_{0.2}\text{Sr}_{0.4}\text{MnO}_3 \)

Anita D. Souza\(^1\) · Megha Vagadia\(^2\) · Mamatha D. Daivajna\(^1\)

Received: 8 May 2021 / Accepted: 6 August 2021 / Published online: 18 August 2021
© The Author(s) 2021

Abstract
The effect of particle size reduction on the magnetic correlations of \( \text{Pr}_{0.4}\text{Bi}_{0.2}\text{Sr}_{0.4}\text{MnO}_3 \) nanoparticles prepared by top-down approach has been studied in detail. It was observed that as the milling time increases from 0 to 240 min, particle size decreases from 160 to 12 nm. Correspondingly it was observed that the ferromagnetic transition temperature (\( T_C \)) drops (264 to 213 K) and saturation magnetization (\( M_S \)) decreases (2.12–0.41 \( \mu_B/\text{f.u.} \)) while coercivity (\( H_C \)) shows a monotonic increase (0.18–1.5 kOe) as the particle size decreases due to increase in milling. The magnetic entropy change (\( \Delta S \)) also decreases (2.41–0.24 J/kg-K) as particle size decreases indicating a strong correlation between magnetism and particle size. The metamagnetic M–H response of the bulk sample, which signifies the magnetic phase coexistence, is suppressed, and the nature of magnetic interactions demonstrates a transition from long range to short range. The observed characteristics emphasizes that with particle size reduction there is an increase in the surface disorder which can be explained by considering the core–shell model for the nanoparticles.

\* Megha Vagadia
mvagadia@iiserb.ac.in; meghavagadia@gmail.com

\* Mamatha D. Daivajna
mamatha.daijna@manipal.edu

\(^1\) Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka 576104, India

\(^2\) Department of Physics, Indian Institute of Science Education and Research, Bhopal, Madhya Pradesh 462066, India
1 Introduction

The understanding of magnetism at nanoscale is scientifically attractive not only because the quantum mechanical properties of the individual spins become significant, but also for the emergence of new phenomena from confinement and proximity, such as giant magnetoresistance (GMR), spintronics, and superparamagnetism [1–4]. The significant advances in the availability of strategies for the synthesis and characterization of materials have led to the massive interest in magnetic nanoparticles. Currently, magnetic nanostructures such as nanodisc, nanotubes, nanorods, nanowires, and nanocomposites are widely used as active components in magnetic refrigeration, magnetic diagnosis, drug delivery, catalysis, ferrofluids, sensors, energy storage, logic circuits, etc. [5–8]. Apart from the above, manipulating the size and shape of the nanostructures place them close to the biological entity such as gene, protein, and cell. This offers an upper hand for magnetic nanoparticles in biomedical applications such as magnetic hyperthermia, magnetic resonance imaging, tissue engineering, cell tracking, and bioseparation [9, 10]. Additionally, the large surface of the magnetic nanostructures finds potential application in wastewater treatment as nanoabsorbent, energy harvesting, heat transfer, ferrofluids, photocatalysis, pigmentation, etc. [11–16].

The two key factors which dominate the magnetic properties of nanoparticles are the finite-size effects and the surface effects [5, 7]. Finite-size effects result from the quantum confinement of electrons such as single-domain limit and superparamagnetic limit, while the surface effects are related to symmetry breaking of the crystal structure at the boundary. The large fraction of atoms residing at the surface of the nanoparticle control the surface interface effects [4, 5, 7].

In perovskite rare earth manganites, nanoparticles display exotic features such as superparamagnetism, spin glass behaviour, low-field saturation magnetization, low-field magnetoresistance, and large coercivity which are different from their bulk counterparts [17, 18]. These striking characteristics make them suitable for application in magnetic hyperthermia, solid oxide fuel cells, magnetic memory devices, spintronic devices, and magnetic sensors [18]. The feasibility to tune the magnetic transition spread over a broad temperature range and the melting of the robust charge ordering (CO) state in the nanoparticles enable their...
finite-size effects on the evolution of magnetic correlations and magnetocaloric properties…

Among rare earth manganites, Pr$_{1-x}$Sr$_x$MnO$_3$ has attracted extra attention owing to its resemblance to the prototype La$_{1-x}$Sr$_x$MnO$_3$ (LSMO). The parent compound PrMnO$_3$ is an antiferromagnetic (AFM) insulator with $T_N \approx 100$ K. Systematic replacement of Pr$^{3+}$ by Sr$^{2+}$ (i.e. Pr$_{1-x}$Sr$_x$MnO$_3$) changes the magnetic ground state and the system exhibits a second order paramagnetic (PM) to ferromagnetic (FM) transition for Sr$^{2+}$ content $0.20 \leq x \leq 0.45$ [22–24]. In the present study, we focus our attention on Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ (PSMO)-derived composition. PSMO is a room temperature metallic FM with $T_C = 310$ K, $T_M = 260$ K and exhibits moderate magnetoresistance (MR) of 40% for $H = 80$ kOe [25, 26]. It is reported to undergo a structural transition from orthorhombic structure (space group $Pnma$) to monoclinic (space group $I2/a$) structure at $(T_g) \approx 88$ K [27]. It shows both normal and inverse magnetocaloric effect (MCE) in the same sample which is interesting from a practical application point of view as magnetic cooling can be achieved from both adiabatic magnetization and demagnetization in different temperature ranges [26, 28].

Contrary to PrMnO$_3$, BiMnO$_3$ is an FM insulator with $T_C = 100$ K and crystallizes in a monoclinic structure [29, 30]. Sr$^{2+}$ substitution for Bi$^{3+}$ (i.e. Bi$_{1-x}$Sr$_x$MnO$_3$) reduces FM and induces charge ordered (CO) AFM for wide concentration of Sr$^{2+}$ (i.e. $0.25 \leq x \leq 0.80$) [31, 32]. Bi$_{0.75}$Sr$_{0.25}$MnO$_3$ is a well-known CO-AFM showing the highest CO temperature, $T_{CO} = 625$ K among manganites which is robust and stable in an external field as high as 30 T [31, 33]. For $x = 0.40$, i.e. Bi$_{0.6}$Sr$_{0.4}$MnO$_3$ (BSMO), the compound shows a PM-to-AFM transition at $T_N = 150$ K and CO transition at $T_{CO} \approx 600$ K [31, 33]. Previous reports on Bi$^{3+}$-doped LaSrMnO$_3$ [34, 35], LaCaMnO$_3$ [36, 37], PrSrMnO$_3$ [38, 39] demonstrate a transition in the magnetic ground state from FM metallic to AFM insulating with competitive coexistence of FM and AFM clusters for intermediate concentration of Bi$^{3+}$ [34–39]. Across the phase coexistence, the material exhibits a large MR ($\approx 100\%$) and MCE probably due to the melting of the CO state. In the partial doping concentration of Bi$^{3+}$, the system shows predominantly FM features with a systematic drop in $T_C$ and net magnetization [34–39]. However, in the case of NdSrMnO$_3$ [40], NdCaMnO$_3$ [41], Bi$^{3+}$ doping drives the system to be robust CO. The observed unusual behaviour of bismuth manganites is attributed to the presence of $6s$ lone pair electrons in the outermost orbital of Bi$^{3+}$ [42].

In view of the contrasting properties of PSMO and BSMO, in the present work, the effect of particle size reduction on the magnetic properties of 20% Bi$^{3+}$-doped Pr$_{0.8}$Sr$_{0.4}$MnO$_3$ (PSMO) is investigated in detail. 20% Bi$^{3+}$ when substituted in the case of FM La$_{0.2}$Sr$_{0.3}$MnO$_3$, retains dominant FM state both in the bulk form and in the nanoparticles [43]. However, in the case of FM LaCaMnO$_3$ [37, 44] and PrSrMnO$_3$ [39], AFM and FM phase separation has been noticed. Previous reports on Bi-substituted PSMO [38, 39, 45] reveal that for partial Bi$^{3+}$ substitution $T_C$ reduces and MR improves. For a higher concentration of Bi$^{3+}$, multiple magnetic interactions are observed [39]. In our previous studies on magnetic phase coexistence, the Bi$^{3+}$-substituted LSMO nanoparticles reveal an overall drop in net magnetization with size reduction while the metamagnetic M–H behaviour of the system remains significantly unaltered [46–48]. Contrary to that, we find in the present study the suppression in the metamagnetic M–H response with the decrease in particle size. Therefore, a detailed study of the present system was warranted, and we here present our analysis of X-ray diffraction studies and magnetization data discuss the results to reveal the role of particle size reduction on the structure, magnetization, magnetic correlations, and magnetocaloric effect (MCE) of Pr$_{0.4}$Bi$_{0.2}$Sr$_{0.4}$MnO$_3$ nanoparticles.

## 2 Experimental details

Pr$_{0.4}$Bi$_{0.2}$Sr$_{0.4}$MnO$_3$ (PB20SMO) nanoparticles have been prepared using a top-down approach in a two-step process. Initially, polycrystalline bulk samples were prepared by the solid-state reaction of Pr$_6$O$_{11}$, Bi$_2$O$_3$, SrCO$_3$, and MnO$_2$ (all 99.9% purity) weighed stoichiometrically according to the following equation.

\[
(0.067 \ Pr_6 O_{11}) + (0.1 \ Bi_2 O_3) + (0.4 \ SrCO_3) + MnO_2 \rightarrow Pr_{0.4}Bi_{0.2}Sr_{0.4}MnO_3 + xCO_2 (\uparrow)
\]

These oxides were mixed thoroughly using agate mortar pestle with the help of isopropyl alcohol, to get a homogeneous mixture. The obtained mixture was calcined at 800 °C, 900 °C, and 1000 °C, respectively, for 24 h each with intermediate grinding. The powders were then pressed into rectangular pellets and were sintered at 1100 °C for 24 h.

In the second step, the pellets were then crushed into a fine powder and were subjected to high-energy planetary ball milling to prepare nanoparticles. The powders were taken in tungsten carbide jars of 50 ml volume along with 10 mm tungsten carbide balls such that the ball mass-to-sample mass ratio was maintained as 20:1. The ball milling was performed at the main disc speed of 300 rpm. The milling time was varied from 0 to 240 min, and a small quantity of sample was taken out a certain interval of time up to 240 min.

The obtained nanoparticles are characterized for their crystal structure and phase purity using room temperature X-ray diffraction (XRD) measurements taken on a M/s. Bruker D2 Phaser powder X-ray diffractometer with Cu-Kα.
radiation in the 2θ range of 20°–80° with a step size of 0.02°. Magnetic measurements were taken on a M/s quantum design, superconducting quantum interference device (SQUID)-based vibrating sample magnetometer (VSM) in magnetic fields up to ±70 kOe and in the temperature range 2–380 K.

3 Results and discussions

3.1 Room temperature X-ray diffraction

Figure 1a shows the room temperature XRD patterns of bulk and ball-milled PB20SMO samples. The XRD peaks display a systematic broadening with increase in milling time ($t_m$), suggesting reduction in particle size ($D$) and concomitant inducement of microstrain ($\epsilon$) in the lattice. The full width at half maximum (FWHM) of the selected reflections, i.e. (1 2 1), (2 0 2), and (0 4 2), plotted as a function of $t_m$ (Fig. 1b) shows a sudden rise in the value during the beginning of ball milling compared to higher $t_m$. This indicates a substantial drop in $D$ occurs during the initial phase of ball milling compared to higher $t_m$.

To derive the structural parameters, the obtained XRD patterns have been subjected to Rietveld refinement method using the FullProf program [49]. Figure 1c shows the XRD profiles for selected PB20SMO-t ($t$ = 0, 20, 120, and 240 min) along with the pattern calculated through Rietveld refinement method. The XRD patterns have been indexed considering the orthorhombic structure in Pnma space group. As all the Bragg peaks could be indexed using this structure, contamination in the sample during ball milling can be ruled out. This indicates that all the samples studied here are of single phase. The unit cell parameters and reliability values of Rietveld refinement are summarized in Table 1.

For better estimation of $D$ and $\epsilon$ using XRD, the instrumental resolution file (IRF) was obtained by measuring a NIST standard sample (corundum), before starting the Rietveld refinement of PB20SMO. For subsequent PB20SMO samples, only the quantities influenced by the sample properties were refined. The TCH pseudo-Voigt peak shape function [50] was considered for both standard and our samples. On supplying the IRF file during Rietveld refinement, Fullprof generates a volume average of particle size ($D$) and microstrain ($\epsilon$) through the integral breadth method in a microstructure file (*.mic file) [50]. Figure 2 shows the variation in $D$ and $\epsilon$ as a function of $t_m$. A sudden drop in the $D$ has been noticed as the $t_m$ changes from 0 to 60 min while the $\epsilon$ exhibits monotonous increment up to 150 min of ball milling and then tends to saturate. The substantial drop in $D$ could be attributed to the enhanced rate of dislocation densities ($\delta$) and defects induced due to the constant collision between the sample mass and balls with the walls of the jar [51, 52]. From $D$, an estimation of $\delta$ can be obtained from the relation $\delta = \frac{1}{D^2}$ [53]. Inset in Fig. 2 shows the variation in $\delta$ with $t_m$. As $t_m$ increases from 0 to 240 min, $\delta$ shows substantial increase from $10^{13}$ to $10^{15}$ lines/m². Also, since the dimension of the feed size before ball milling is larger compared to after each milling process, the relative particle size decreases with increasing milling time. The characteristic Bragg peaks are indexed using PXRD patterns of bulk and ball-milled PB20SMO samples.
Finite-size effects on the evolution of magnetic correlations and magnetocaloric properties...

Table 1 Rietveld refined unit cell parameters and reliability values of Rietveld refinement of X-ray diffraction patterns for PB20SMO-t refined using orthorhombic structure, space group Pnma

| Parameter          | t = 0 min | t = 20 min | t = 120 min | t = 240 min |
|--------------------|-----------|------------|-------------|-------------|
| a (Å)              | 5.46801 (27) | 5.46894 (27) | 5.48661 (178) | 5.48438 (238) |
| b (Å)              | 7.68497 (34) | 7.67849 (25) | 7.64509 (80)   | 7.63690 (117) |
| c (Å)              | 5.49744 (25) | 5.50121 (26) | 5.50932 (196)  | 5.51168 (263) |
| V (Å³)             | 231.011 (19) | 231.014 (18) | 231.092 (114)  | 230.849 (153) |
| R_p                | 14.5       | 11.0       | 9.15         | 7.52         |
| R_wp               | 20.0       | 14.5       | 11.8         | 9.70         |
| R_exp              | 11.48      | 9.01       | 9.44         | 9.06         |
| χ²                 | 3.05       | 2.59       | 1.55         | 1.14         |
| Bragg R Factor     | 8.22       | 5.72       | 3.64         | 2.54         |
| Particle size (D) (nm) | 160       | 36         | 17           | 12           |
| Microstrain (ε) × 10⁻⁴ | 26.33     | 31.26      | 90.21        | 100.09       |
| Dislocation density (δ) × 10¹³ (lines/m²) | 0.039 | 0.771 | 3.460 | 6.944 |
| Degree of crystallinity (%) | 92.64 | 90.91 | 74.46 | 66.01 |

Fig. 2 The variation of particle size and microstrain is shown as a function of milling time for PB20SMO. Inset shows the variation in dislocation density with milling time.

Figure 3 shows the dc magnetization plots for PB20SMO-D samples (D = 160, 36, 17, 12 nm) in the temperature range of 3–380 K in an applied field of 100 Oe. The magnetization has been recorded under zero field-cooled (ZFC) and field-cooled (FC) state of the samples. All samples show a huge drop in D and a rise in ε is witnessed during the initial phase of ball milling. Further, the degree of crystallinity (DC) has been estimated using the relation

\[ \text{DC} = \frac{\text{Area of crystalline peaks}}{\text{Area of all peaks} (\text{crystalline} + \text{amorphous})} \]

DC decreases from 92 to 66% as \( t_m \) increases (Table 1). Thus, based on the estimated D from XRD, four samples obtained after \( t_0, 20, 120, \) and 240 min of ball milling having particle size \( D = 160, 36, 17, \) and 12 nm, respectively, were chosen to study, in detail, the influence of particle size reduction on the magnetic properties.

3.2 Magnetization studies

The line connecting the points is a guide to eyes. Inset in 3 b shows temperature variation of \( M_{ZFC} - M_{FC} \).
well-defined PM-to-FM transition ($T_C$) which drops from 264 K for $D = 160$ nm to 210 K for $D = 12$ nm (inset (ii) in Fig. 3a). Compared to PSMO which has $T_C = 308$ K [28, 54], 20% Bi$^{3+}$ substitution reduces the $T_C$ to 264 K. Also, the low-temperature structural transition which was seen as a drop in ZFC and FC curve for PSMO [26, 28] is suppressed with Bi$^{3+}$ substitution. However, the bulk PB20SMO-160 ($D = 160$ nm) sample shows a hump in FC at $T \leq 200$ K which could be attributed to the disordered antiferromagnetic (AFM) interactions in the system. Similar low-temperature hump in FC curve has been noticed in case of La$_{0.7}$-Bi$_{0.3}$Sr$_{0.3}$MnO$_3$ ($x = 0.30$ and 0.35) [46, 48, 55]. The decrease in $T_C$ with Bi$^{3+}$ substitution can be explained considering the increase in unit cell volume. As seen from the XRD analysis, the unit cell volume increases from 229.214 to 231.011 Å$^3$ as $x$ changes from 0 to 0.20 [54]. This elongates the Mn–O–Mn chains, thus reducing the hopping of $e_g$ electrons. The double exchange coupling weakens, thereby resulting in the decrease of $T_C$. Also, the highly covalent 6s lone pair character of Bi$^{3+}$ is expected to create localization of electrons around the Bi$^{3+}$-rich region which leads to AFM coupling, thereby decreasing the FM character of PSMO.

Further, the sharp magnetic transition recorded for the bulk sample broadens with the decrease in $D$ which can be seen as the increase in the FWHM of $dM/dT$ curve (inset (ii) in Fig. 3a). This may be due to the weak magnetic interaction among the spins on the surface of the nanoparticles. Also, a large bifurcation between ZFC and FC curves noticed in all samples specifies the presence of inhomogeneity in the system. The strength of the inhomogeneity can be quantified as $M_{FC} - M_{ZFC}$ (inset in Fig. 3b) which is higher for PB20SMO-36 and PB20SMO-17 samples.

The high-temperature inverse magnetic susceptibility ($\chi^{-1}$) has been analysed using the Curie–Weiss (CW) law [56], $\chi = \frac{C}{T - \theta_p}$, C is Curie’s constant, and $\theta_p$ is Curie–Weiss temperature. Figure 4 shows the $\chi^{-1}$ vs $T$ plots for PB20SMO-D. From the slope of the linear fit in the temperature range $310 \leq T \leq 380$ K, the values of $\theta_p$ have been determined. Inset in Fig. 4 shows the $\theta_p$ vs $D^{-1}$ plot. The positive values of $\theta_p$ demonstrate the dominant FM interactions in the system. With a decrease in $D$, the $\theta_p$ value decreases suggest a weakening of FM interaction with size reduction. Additionally, it is interesting to note that all samples show a deviation from the CW behaviour exhibiting a downturn, below a certain temperature ($T_G$) in each sample’s case. This may be accounted as the presence of short-range FM correlations above $T_C$. Most reports assign this anomaly to the Griffith’s like singularity in the system [57–60] while some literature suggests the presence of FM polarons above $T_C$ could result in $\chi^{-1}(T)$ downturn [61–63]. In general, the existence of GP like behaviour is characterized by a downturn in $\chi^{-1}(T)$, which is sharp for lower applied fields and subdues with an increase in the magnitude of applied magnetic field. Also, the low field $\chi^{-1}$ shows a temperature dependence given by the power law [57],

$$\chi^{-1} \propto (T - T_C^{-\frac{R}{T}})^{(1-\lambda)} \quad 0 \leq \lambda \leq 1 \quad (1)$$

where $T_C^R$ is the critical temperature of a random ferromagnet and the exponent $\lambda$ determines the deviation from CW law. The temperature at which $\chi^{-1}(T)$ deviates from linearity is known as Griffith’s temperature, $T_G$. The $T_G$ in the present case decreases with a decrease in particle size. Figure 5 shows the $\chi^{-1}$ vs T plots in different applied magnetic fields for PB20SMO-D. A systematic softening of the downturn has been noticed with an increase in the magnitude of applied magnetic field. This may be understood as in higher applied fields the magnetic contribution from PM matrix enhances and dominates the embedded FM clusters, hence driving towards linear variation in $\chi^{-1}$ vs T. Using the procedure described in Ref [57], the value of $\lambda$ has been estimated from the plot of $\chi^{-1} - [T/ T_C^{-R}] - 1$ in double logarithmic scale (inset in each panel of Fig. 5). The slope of the linear fit gives the value of $\lambda$ tabulated in Table 2. The estimated value of $\lambda$ is in good agreement with the reported literature [57–60], thereby suggesting the applicability of GP model to explain the deviation in $\chi^{-1}(T)$. Also, the magnitude of $\lambda$ is found to increase with particle size reduction implying the enhancement in the strength of GP like singularity. On the contrary, Souza et al. [61] suggested that GP like treatment
Finite-size effects on the evolution of magnetic correlations and magnetocaloric properties...

for accounting the $\chi^{-1}(T)$ downturn is inappropriate and proposed the presence of FM polarons, intrinsic to manganites due to structural and chemical disorder to be responsible to $\chi^{-1}(T)$ deviation from CW behaviour. Later, Rozenberg et al. [64, 65] and Aga Shahee et al. [66] supported the above hypothesis. Since conductivity in manganites above $T_M$ is accounted by the hopping of small polarons, it appears as if both the proposed models hold. However, the magnitude of resistivity and polaron activation energy $E_a$ of a ferromagnetic manganite is found to increase with a decrease in $D$ [67–69], thus suspecting the applicability of the FM polarons hypothesis.

To gain deeper insights into the magnetic interactions, field-dependent isothermal magnetization loops were recorded for PB20SMO-$D$ at different temperatures (Fig. 6a–d). For PB20SMO-160, the $M$–$H$ behaviour at 300 K is nonlinear and unsaturated suggesting the presence of weak magnetic interactions in the system. On lowering the temperature to $T < T_C$, i.e. 200 K, the $M$–$H$ response shows a significant spontaneous moment ($M_0$) with unsaturated magnetization suggesting the coexistence of FM and AFM interactions in the system. At $T = 100$ K and 50 K, the $M$–$H$

![Fig. 5](https://example.com/fig5.png)

**Fig. 5** A plot of temperature evolution of inverse magnetic susceptibility in different magnetic fields for PB20SMO. Inset in each panel shows inverse susceptibility versus $[(T/T_C)^2]^{-1}$ in double logarithmic scale and solid line represent the linear fit.

**Table 2** Values of $T_C$, $\theta_p$, $T_G$, $\lambda_{pm}$, $\lambda_{gp}$, and other calculated microstructural parameters for bulk and ball-milled PB20SMO samples

| Sample (PB20SMO-$D$) | $D = 160$ | $D = 36$ | $D = 17$ | $D = 12$ |
|----------------------|-----------|-----------|-----------|-----------|
| $T_C$ (K)            | 264       | 256       | 237       | 213       |
| $\theta_p$ (K)       | 256       | 246       | 191       | 129       |
| $T_G$ (K)            | 310       | 310       | 304       | 300       |
| $\lambda_{pm}$       | 0.02      | 0.09      | 0.06      | 0.04      |
| $\lambda_{gp}$       | 0.86      | 0.86      | 0.92      | 0.95      |
| $M_0 - 3$ K (μB/f.u.)| 2.12 (02) | 1.82 (001)| 0.87 (002)| 0.41 (003)|
| $a$ (3 K, kOe)       | 0.25 (0.01)| 0.26 (0.01)| 1.53 (0.04)| 1.82 (0.07)|
| $b$ (3 K, kOe$^2$)   | 4.13 (0.06)| 2.79 (0.07)| 2.47 (4)   | 2.71 (0.21)|
| $\chi_p \times 10^{-5}$ (3 K) | 351 (2) | 388 (2) | 593 (2) | 636 (6) |
| $K \times 10^3$ (3 K) erg/cm | 2.09 | 1.47 | 0.67 | 0.33 |
| Shell thickness ($t$) (nm) | – | 1.47 | 2.53 | 2.62 |

![Fig. 6](https://example.com/fig6.png)

**Fig. 6** Field-dependent magnetization plots for PB20SMO-$D$, a $D = 160$ nm, b $D = 36$ nm, c $D = 17$ nm, and d $D = 12$ nm at different temperatures
loops represent distinct behaviour with open loops along the positive and negative field sweep. The magnetization in the virgin loop remains unsaturated even in the field as high at 70 kOe with notable spontaneous moment signifying the alignment of residual FM domains parallel to the applied magnetic field. In the reverse field sweep (demagnetization curve), the sample remains in a high state down to 10 kOe and then rapidly drops to zero at \( H = 0 \) kOe. In the negative field sweep, a response similar to the positive field sweep has been noticed; however, the area under the loop along with the forward and reverse field sweep is less compared to the positive field sweep. The observed M–H response implies the presence of metamagnetic magnetization with the ramping field. This suggests field-induced AFM-to-FM transition in the system. At \( T = 3 \) K, a clear step like feature has been observed in the virgin curve at critical field \( H_C = 50 \) kOe. Along the demagnetization path, the system remains in a high magnetic state down to 9 kOe field and then drops to zero at zero field. When the field is increased in the negative direction, the magnetization curve is similar to the demagnetization curve of the positive field and follows a similar pathway with further field sweep. This indicates that the field-induced transition from the AFM to FM state is irreversible and the induced FM phase is stable at this temperature. The net magnetization at 3 K is less compared to that at 50 K and 100 K and indicates an increase in the volume fraction of AFM interactions at 3 K.

For PB20SMO-36, the recorded magnetization with the ramping field is similar to that of PB20SMO-160 but a small drop in the open-loop area has been noticed. In the case of PB20SMO-17 and PB20SMO-12, the M–H is highly unsaturated signifying the increased surface disorder that leads to the reduced magnetic interaction. Also, it is interesting to note that the difference between the virgin curve and loop which was clearly identified in the bulk sample tend to merge in ball-milled sample implying the increase in the volume fraction of AFM interactions in the nanoparticles. Further, the net magnetization has been found to systematically increase with a decrease in temperature contrary to PB20SMO-160 and PB20SMO-36.

Figure 7 shows the temperature evolution of (a) saturation magnetization \((M_s)\) and (b) coercivity \((H_C)\). On lowering the temperature from 300 K, an overall increase in the value of \( M_s \) and \( H_C \) is noticed. The elevation in \( M_s \) with a decrease in \( T \) corroborates the PM-to-FM transition in all the samples while a small drop in \( M_s \) at a lower temperature for \( D = 160 \) and 36 nm ratifies the hump recorded in the FC curve below \( T = 200 \) K for PB20SMO-160 (inset (ii) in Fig. 3a). The \( H_C \) values plotted as a function \( D \) (inset in Fig. 7b) display a rise with a drop in \( D \) due to the increased surface anisotropy because of the lattice strain and broken bonds as the \( D \) comes down [70]. In general, with a decrease in \( D \), \( H_C \) increases and attains a maximum value for a critical particle size \( D_c \) where nanoparticles show a transition from multidomain to single-domain state. For further decrease in \( D \), \( H_C \) drops. Inset in Fig. 7b shows the variation in \( H_C \) vs \( D^{-1} \) fitted to \( H_C = m + n/D \), where \( m \) and \( n \) are constants. Linear variation in \( H_C \) vs \( D^{-1} \) (inset in Fig. 7b) suggests the multidomain nature of the nanoparticles [43, 71].

The law of approach to saturation (LAS) fit [72],

\[
M = M_s \left(1 - \frac{a}{H} - \frac{b}{H^2}\right) + \chi_p H
\]  

(2)
given to the demagnetization curves in the first quadrant provide more insights into the magnetic behaviour. The term \( M_s \) in the above relation refers to the saturation magnetization, \( a/H \) corresponds to the structural defects while \( b/H^2 \) is related to the uniaxial magneto-crystalline anisotropy given as [73] \( K = \frac{15}{4} bM_s^2 \) (erg/cm) and \( \chi_p H \) is the high field susceptibility. Figure 8 shows the LAS fit given to the M–H curves at 3 K and the fitting parameters are summarized in Table 2. A rise in the \( a/H \) values specifies an increase in the structural defects due to ball milling. The estimated \( K \) values are of the order \( 10^5 \) erg/cm\(^3\) and decrease with particle size reduction due to disorder in the core of the nanoparticles. Further a substantial drop in \( M_s \) from 2.1 \( \mu_B/\text{f.u.} \) to 0.2 \( \mu_B/\text{f.u.} \) has been noticed with a drop in \( D \) (Fig. 9). \( M_s \) plotted as a function of \( D^{-1} \) (inset in Fig. 9) shows a linear variation.
specifying a strong impact of particle size on the $M_S$ of the sample.

The range of magnetic interaction with particle size reduction can be interpreted from the $M^2$ vs H/M (i.e. Arrott’s plots) [57, 66]. If the linear interpolation of the high-field-magnetization region of $M^2$ vs H/M yields a positive slope, it represents the presence of spontaneous moment with long-range FM order while the negative slope represents short-range FM correlations in the system. As shown in Fig. 10, the intercept value for PB20SMO-160 and PB20SMO-36 is negative at $T = 300 \, K > T_C$ and positive for $T \leq 200 \, K < T_C$, demonstrating that the magnetic interactions above $T_C$ are short-ranged while those below $T_C$ the system exhibit long-range FM order. Similarly, for PB20SMO-17, the intercept has negative value at $T > 200 \, K$ and transforms to be positive $T < 100 \, K$ signifying a crossover in the range of FM interactions across magnetic ordering. However, for PB20SMO-12, the intercept is negative at all temperatures demonstrate the FM interactions to be short-ranged due to increased surface disorder because to ball milling.

The magnetic entropy change $\Delta S$ has been determined from iso-field magnetization using Maxwell’s thermodynamic relation [74],

$$\Delta S(T, H) = S_M(T, H) - S_M(T, 0) = \frac{H}{\mu_0} \left( \frac{\partial M}{\partial T} \right)_H$$  (3)

where $M$ is the magnetization, $H$ is the applied magnetic field, and $T$ is the temperature. According to Maxwell relation, the change in magnetic entropy upon application of magnetic field is related to magnetization with respect to the temperature through
\[
\left( \frac{\partial S}{\partial H} \right)_T = -\left( \frac{\partial M}{\partial T} \right)_H
\]

Most frequently magnetization isotherms recorded across the \( T_C/T_N \) and specific heat measurements are used to estimate the \( \Delta S \) values [74]. However, some recent reports suggest the estimation of \( \Delta S \) from iso-field magnetization [75, 76]. A close overlap in the estimation of \( \Delta S \) from isothermal and iso-field magnetization validates the application of the latter approach to estimate the MCE. Figure 11 a-d shows the variation of \( \Delta S \) as a function of temperature in different applied fields (i.e. \( H = 10 \) kOe and 50 kOe). As expected, a large change in \( \Delta S \) has been observed in the vicinity of \( T_C \). The bulk PB20SMO shows a maximum entropy change \( \Delta S_M \) of 2.43 J/kg-K for \( H = 50 \) kOe which drops to 0.24 J/kg-K as particle size reduces (table 3) along with broadening of \( \Delta S \) curve. The relative cooling power (RCP) defined as \( \text{RCP} = \Delta S_M \times \delta T_{\text{FWHM}} \), where \( \delta T_{\text{FWHM}} \) is the full width half maximum of \( \Delta S \) curve, also drops with a decrease in the particle size (table 3).

A sudden variation in \( \Delta S \) across \( T_C \) could be accounted for by considering the change in magnetization and the spin–lattice coupling across the magnetic ordering temperature [74]. The variation in the Mn–O–Mn bond angle and Mn–O bond length with temperature results in the volume change, thereby influencing the \( \Delta S \) values. A comparison of the obtained \( \Delta S_M \) with few reported studies is summarized in table 4 [77–84]. The \( \Delta S_M \) value in the present study is less compared to PSMO which indicates that Bi\(^{3+}\) addition suppresses the net magnetization of the system.

From the above results, it can be noticed that with an increase in \( t_m \), the dislocation density and microstrain increase while the degree of crystallinity drops. Correspondingly a decrease in \( T_C, M_S, K, \) and \( \Delta S \) has been observed while \( H_C \) values display a monotonous increase. Also, a transition in the range of magnetic interactions from long range to short range has been noticed. A similar variation in the magnetic properties with a decrease in particle size has been previously reported in the case of manganites [28, 71, 73, 85–88] and other oxides [89–92]. The observed characteristic could be accounted for by considering the core–shell structure of the nanoparticles [93], according to which each nanoparticle has a FM/AFM grain surrounded by a non-magnetic shell comprised of broken bonds and randomly oriented magnetic spins.

Assuming the net magnetization of the shell to be zero, an estimate of shell thickness (\( t \)) can be attained from the relation [94],

\[
t = \frac{D}{2} \left( 1 - \left( \frac{M_S^{\text{(Nano)}}}{M_S^{\text{(Bulk)}}} \right)^{1/3} \right)
\]

where \( D \) is the particle size, \( M_S^{\text{(Bulk)}} \) and \( M_S^{\text{(Nano)}} \) corresponds to the saturation magnetization of bulk and nanoparticles, respectively. The \( M_S^{\text{(Bulk)}} \) value is obtained from the intercept of \( M_S \) vs \( D^{-3} \) plot (inset in Fig. 10). The estimated obtained values of \( t \) are tabulated in Table 2.
shows the variation of $t/D$ (i.e. shell thickness/particle size) as a function of $D$. The $t/D$ ratio increases monotonously with a drop in $D$. A linear dependence of $t/D$ with $D^{-1}$ suggests a direct impact of size reduction on the thickness of the non-magnetic shell that strongly controls the magnetic properties of the nanoparticles.

Since it has been well understood that with a decrease in $D$, the surface effects dominate compared to the core. The growth in dislocation density, vacancies, lattice defects, and low crystallinity adds to the surface defects which increases the separation between the FM core. This, in turn, reduces the magnetic interaction among them resulting in the drop of net magnetization, $T_c$ and $\Delta S_M$ with broad magnetic transitions. However, the metamagnetic magnetization loops noticed for bulk and ball-milled PB20SMO demonstrate the observed behaviour to be a characteristic of magnetic interaction among the cores. Since it has been well established that PSMO is a metallic FM [12] and BSMO is a CO-AFM [16], PB20SMO represents a solid solution in both parent phases, thus showing the magnetic state of both phases. Similar coexistence of FM and AFM phases has been reported in case of Bi-substituted LaCaMnO$_3$ [22, 34], LaSrMnO$_3$ [20, 41], NdSr/CaMnO$_3$ [25, 26] for a particular concentration of Bi$^{3+}$. Even though Bi$^{3+}$ is diamagnetic and the Mn$^{3+}$/Mn$^{4+}$ concentration is unaltered with Bi$^{3+}$ substitution, the presence of 6$s$ lone pair electrons of Bi$^{3+}$ leads to the localization of charges across the Bi–O bonds. The antiparallel spin orientation between localized electrons and Mn$^{3+}$/Mn$^{4+}$ results in AFM superexchange coupling between Mn–O–Mn chains around Bi$^{3+}$-rich regions, thereby driving the system towards AFM.

Further, the scientific conflict in assigning the sharp downturn observed in $\chi^{-1}(T)$ to either GP like singularity or the presence of FM polarons demands the presence of quenched disorder in the system [43–53]. Generally, in most of the manganites, $A$-site substitution that leads to the structural distortion due to the tilting of MnO$_6$ octahedra is expected to be the cause of quenched disorder while some reports suggest the competitive coexistence of the FM and AFM phases [44] and the magnetic interactions among the different magnetic ions due to $B$-site substitution [43] also results in quenched disorder. In the present case, the tilting of MnO$_6$ octahedra along with FM and AFM phase coexistence due to Bi$^{3+}$ ions could be considered as the source of quenched disorder in bulk PB20SMO. Additionally, the broken Mn–O–Mn network due to ball milling also adds to the quenched disorder in PB20SMO nanoparticles. The local FM fluctuations resulted from the random spatial variation

### Table 4

A comparison of $\Delta S_M$ and RCP values for different samples

| Compound                                      | $T_C$ (K) | $H$ (kOe) | $\Delta S_M$ (J/kg-K) | RCP (J/kg) | Ref   |
|-----------------------------------------------|-----------|-----------|-----------------------|-----------|-------|
| Pr$_{0.55}$Sr$_{0.45}$MnO$_3$                 | 300       | 30        | 1.71                  | 143.64    | 77    |
| Pr$_{0.6}$Sr$_{0.4}$MnO$_3$                   | 321       | 25        | 2.3                   | 35.5      | 78    |
| Pr$_{0.6}$Sr$_{0.4}$MnO$_3$                   | 310       | 60        | 3.9                   | 56        | 79    |
| La$_{0.37}$Bi$_{0.63}$Ba$_{0.33}$MnO$_3$      | 229       | 50        | 3.42                  | 260       | 80    |
| La$_{0.47}$Bi$_{0.53}$Ba$_{0.33}$MnO$_3$      | 270       | 50        | 3.88                  | 236       | 80    |
| La$_{0.75}$Bi$_{0.25}$Ba$_{0.30}$MnO$_3$      | 300       | 40        | 3.41                  | 180.16    | 81    |
| La$_{0.8}$Bi$_{0.2}$Sr$_{0.05}$(Ca$_{0.55}$Ba$_{0.45}$)$_{0.12}$MnO$_3$ | 140 | 20 | 1.62 | 136 | 82 |
| La$_{0.8}$Bi$_{0.2}$Sr$_{0.05}$(Ca$_{0.55}$Ba$_{0.45}$)$_{0.12}$MnO$_3$ | 195 | 10 | 0.51 | - | 83 |
| La$_{0.8}$Sr$_{0.2}$MnO$_3$                   | 115       | 10        | 0.47                  | -         | 83    |
| Pr$_{0.5}$Bi$_{0.5}$Sr$_{0.2}$MnO$_3$         | 140       | 50        | 3.11                  | 196.39    | 84    |
| Pr$_{0.5}$Bi$_{0.5}$Sr$_{0.3}$MnO$_3$         | 210       | 50        | 5.41                  | 197.95    | 84    |
| Pr$_{0.5}$Bi$_{0.5}$Sr$_{0.3}$MnO$_3$, $D=160$ nm | 264   | 50        | 2.41                  | 190.01    | Present work |
| Pr$_{0.5}$Bi$_{0.5}$Sr$_{0.3}$MnO$_3$, $D=36$ nm | 256   | 50        | 1.580                 | 156.46    | Present work |

**Fig. 12** Variation in $t/D$ as a function of particle size ($D$). Inset shows the linear fit given to $t$ vs $D^{-1}$
in the magnetic exchange interactions due to particle size reduction result in the formation of short-range FM domains embedded in the PM matrix.

4 Conclusions

Systematic analysis of the magnetization data has been carried out to understand the role of particle size reduction on the magnetic correlations and magnetocaloric properties of Pr0.4Bi0.2Sr0.4MnO3. As the particle size decreases from 160 to 12 nm, T_C drops from 264 to 213 K along with a drastic reduction in the net magnetization from 2.12 to 0.41 μ_B/f.u. and ΔSM from 2.43 to 0.24 J/kg-K. Correspondingly a suppression in the metamagnetic M–H loops has been observed which suggests a reduced magnetic interaction among the nanoparticles. The observed properties can be explained due to the formation of a non-magnetic shell around the FM/AFM core. Additionally, a sharp downturn noticed in the inverse susceptibility suggests the presence of short-range FM correlations above T_C.

Acknowledgements AD is indebted to the Department of Science and Technology, India, for financial support through the INSPIRE Fellowship (IF 170553). MV acknowledges the Department of Science and Technology, India, for the INSPIRE faculty award (DST/INSPIRE/04/2017/003059). The authors are thankful to Dr. S. Rayapol (UGC-DAE-CSIR, Mumbai) for fruitful discussions, M. Venugopal (UGC-DAE-CSIR, Mumbai) for help in high-energy planetary ball milling and XRD measurements, and Mr. Manoj Prajapat for help in magnetic measurements.

Author’s contribution ADS carried out conceptualization, formal analysis, and investigation, and wrote the original draft. MV performed validation, resources, writing, reviewing, and editing. MD was involved in supervision, writing, reviewing, and editing. MD was involved in supervision, writing, reviewing, and editing.

Funding Open access funding provided by Manipal Academy of Higher Education, Manipal.

Data availability The data set analysed in the current study could be available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflict of interests.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.

References

1. M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Eitenne, G. Creuzet, A. Friederich, J. Chazelas, Giant magnetoresistance of (001) Fe/(001) Cr magnetic superlattices. Phys. Rev. Lett. 61, 2472 (1988)
2. I. Žutić, J. Fabian, S.D. Sarma, Spintronics: Fundamentals and applications. Rev. Mod. Phys. 76, 323 (2004)
3. C.P. Bean, U.D. Livingston, Superparamagnetism. J. Appl. Phys. 30, 1210 (1959)
4. R. Wiesendanger, (ed) Atomic- and Nanoscale Magnetism. Springer International Publishing (2018)
5. R.H. Kodama, Magnetic nanoparticles. J. Magn. Magn. Mater. 200, 359 (1999)
6. G. Reiss, A. Hütten, Applications beyond data storage. Nat. Mater. 4, 725 (2005)
7. S.P. Gubin, (ed) Magnetic nanoparticles. Wiley (2009)
8. L. Mohammed, H.G. Gomaa, D. Ragab, J. Zhu, Magnetic nanoparticles for environmental and biomedical applications: A review. Particuology 30, 1 (2017)
9. I.M. Anik, M.K. Hossain, I. Hossain, I. Ahmed, R.M. Doha, Biomedical applications of magnetic nanoparticles. In Magnetic Nanoparticle-Based Hybrid Materials. Woodhead Publishing, pp. 463–497 (2021)
10. Y. Xiao, J. Du, Superparamagnetic nanoparticles for biomedical applications. J. Mater. Chem. B 8, 354 (2020)
11. S. Odenbach, ed., Ferrofluids: magnetically controllable fluids and their applications. Springer, p 594 (2008)
12. F. Almomani, R. Bhosale, M. Khraisheh, T. Almomani, Heavy metal ions removal from industrial wastewater using magnetic nanoparticles (MNP). Appl. Surf. Sci. 506, 144924 (2020)
13. F.S.A. Khan, N.M. Mubarak, M. Khalid, R. Walvekar, E.C. Abdullah, S.A. Mazari, S. Nizamuddin, R.R. Karri, Magnetic nanoadsorbents’ potential route for heavy metals removal-a review. Environ. Sci. Pollut. Res. 27, 24342 (2020)
14. M.L. Seol, S.B. Jeon, J.W. Han, Y.K. Choi, Ferrofluid-based triboelectric–electromagnetic hybrid generator for sensitive and sustainable vibration energy harvesting. Nano Energy 31, 233 (2017)
15. T. Dippong, E.A. Levei, F. Goga, I. Petean, A. Avram, O. Cadar, The impact of polyol structure on the formation of Zn0.6Co0.4Fe2O4 spinel-based pigments. J Sol-Gel Sci Technol 92, 736 (2019)
16. T. Dippong, E.A. Levei, C.L. Lengauer, A. Daniel, D. Toloman, O. Cadar, Investigation of thermal, structural, morphological and photocatalytic properties of Cu1/nCo1–nFe2O4 (0 ≤ x ≤ 1) nanoparticles embedded in SiO2 matrix. Mater. Charact. 163, 110268 (2020)
17. V. Markovich, A. Wisniewski, H. Szymczak, Magnetic properties of perovskite manganites and their modifications. In Handbook of Magnetic Materials. Elsevier, vol. 22, 1 (2014)
18. W. Xia, Z. Pei, K. Leng, X. Zhu, Research progress in rare earth-doped perovskite manganite oxide nanostructures. Nanoscale Res. Lett. 15, 1 (2020)
19. T. Zhang, X.P. Wang, Q.F. Fang, X.G. Li, Magnetic and charge ordering in nanosized manganites. Appl. Phys. Rev. 1, 031302 (2014)
20. M.H. Phan, S. Chandra, N.S. Bingham, H. Srikanth, C.L. Zhang, S.W. Cheong, T.D. Hoang, H.D. Chinh, Collapse of charge ordering and enhancement of magnetocaloric effect in nanocrystalline La0.33Pr0.275Ca0.375MnO3. Appl. Phys. Lett. 97, 242506 (2010)
21. X. Huang, T.R. Paudel, S. Dong, E.Y. Tsyshbaly, Hexagonal rare-earth garnet magnets as promising photovoltaics and light polarizers. Phys. Rev. B 92, 125201 (2015)

22. K. Knizk, Z. Jirak, E. Pollert, F. Zounova, S. Vratislav, Structure and magnetic properties of Pr$_{1-y}$Sr$_y$MnO$_3$ perovskites. J. Solid State Chem. 100, 292 (1992)

23. D. Sánchez, J.A. Alonso, M.J. Martínez-Lope, Neutron-diffraction study of the Jahn-Teller transition in PrMnO$_3$. J. Chem Soc. Dalton Trans 23, 4422 (2002)

24. O. Chmaissem, B. Dabrowski, S. Kolesnik, J. Mais, J.D. Jorgensen, S. Short, Structural and magnetic phase diagrams of La$_{1-x}$Sr$_x$MnO$_3$ and Pr$_{1-y}$Sr$_y$MnO$_3$. Phys. Rev. B 67, 094431 (2003)

25. W. Boujelben, M. Ellouze, A. Cheikh-Rhouhou, J. Pierre, Q. Cai, W.B. YeLon, K. Shimizu, C. Dubourdieu, Neutron diffraction, NMR and magneto-transport properties in the Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ perovskite manganite. J. Alloys Compd. 334, 3 (2002)

26. D.V. Maheswar Repaka, T.S. Tripathi, M. Aparnadevi, R. Mahendiran, Magnetocaloric effect and magnetothermopower in the room temperature ferromagnet Pr$_{0.6}$Sr$_{0.4}$MnO$_3$. J. Appl. Phys. 112, 123915 (2012)

27. C. Ritter, P.G. Radaelli, M.R. Lees, J. Baratt, G. Balakrishnan, D. McK Paul, A new monoclinic perovskite allototype in Pr$_{0.6}$Sr$_{0.4}$MnO$_3$. J. Solid State Chem. 127, 276 (1996)

28. A.D. Souza, M. Vagadia, M. Daivajna, Tuning magnetic and magnetocaloric properties of Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ through size modifications. J. Mater Sci: Mater Electron 32, 14990 (2021)

29. T. Atou, H. Chiba, K. Ohoyama, Y. Yamaguchi, Y. Syono, Structure determination of ferromagnetic perovskite BiMnO$_3$. J. Solid State Chem. 145, 639 (1999)

30. A. Dos Santos, A.K. Moreira, T. Cheetham, Y. Atou, Y. Syono, K. Yamaguchi, K. Ohoyama, H. Chiba, C.N.R. Rao, Orbital ordering as the determinant for ferromagnetism in biferroic BiMnO$_3$. Phys. Rev. B 66, 064425 (2002)

31. O.S. Mantystayska, I.O. Troyanchuk, A.N. Chobot, H. Szymczak, Magnetic phase diagram of the bismuthites Bi$_{1-x}$Sr$_x$MnO$_3$. Low Temp. Phys. 30, 218 (2004)

32. H. Chiba, T. Atou, Y. Syono, Magnetic and electrical properties of Bi$_{1-x}$Sr$_x$MnO$_3$: hole-doping effect on ferromagnetic perovskite BiMnO$_3$. J. Solid State Chem. 132, 139 (1997)

33. J.L. García-Muñoz, C. Frontera, M. Respaud, M. Giot, C. Ritter, A.D. Souza, S. Rayaprol, M.S. Murari, Mamatha Daivajna, N. Kambhala, M. Chen, L. Peng, X.X. Zhang, D. Rajesh, K.S. Gómez, D. Sánchez-Jiménez, S. Lozano-Pérez, V. Franco, A. Conde, Ball milling as a way to produce magnetic and magnetocaloric materials: a review. J. Mater Sci. 52, 11834 (2017)

34. J.R. Sun, J. Gao, Y. Fei, R.W. Li, B.G. Shen, Doping effects on the phase separation in perovskite La$_{0.67-x}$Bi$_x$Ca$_{0.33}$MnO$_3$. Phys. Rev. B 67, 144414 (2003)

35. I. Kammoun, W. Cheikhrouhou-Koubaa, W. Boujelben, A. Cheikhrouhou, Structural and magnetic properties of Bi doped in the A site of (Pr$_{1-x}$Bi)$_x$Sr$_{0.4}$MnO$_3$ (0 ≤ x ≤ 0.4) perovskite manganites. J. Mater. Sci. 43, 960 (2008)

36. A.D. Souza, S. Rayaprol, M.S. Murari, M. Daivajna, Effect of milling on structure and magnetism of nanocrystalline La$_{0.7-x}$Bi$_x$Sr$_{0.3}$MnO$_3$ (x = 0.35, 0.40) manganites. Physica B Condens. Matter 570, 412792 (2021)

37. A.D. Souza, S. Rayaprol, M. Daivajna, Effect of Bi$_{3+}$ on magnetic properties of nanosized La$_{0.7}$Bi$_{0.3}$MnO$_3$. Mater Today Proc (2021). https://doi.org/10.1016/j.matpr.2020.11.765

38. A.D. Souza, S. Rayaprol, M.S. Murari, M. Daivajna, Effect of Particle Size on Magnetic Phase Coexistence in Nanocrystalline La$_{0.7-x}$Bi$_x$Sr$_{0.3}$MnO$_3$ (Under Review)

39. T. Roisnel, J. Rodríguez-Carvajal, WinPOLOTR: a windows tool for powder diffraction pattern analysis Mater. Sci. Forum 378, 118 (2001)

40. J. Rodríguez-Carvajal, T. Roisnel, Line broadening analysis using FullProf*: determination of microstructural properties. Mater. Sci. Forum 443, 123 (2004)

41. M. Sopicka-Lizer ed., High-energy ball milling: mechanochemical processing of nanopowders. Elsevier (2010)

42. J.S. Blázquez, J.J. Ipus, L.M. Moreno-Ramírez, J.M. Álvarez-Gómez, D. Sánchez-Jiménez, S. Lozano-Pérez, V. Franco, A. Conde, Ball milling as a way to produce magnetic and magnetocaloric materials: a review. J. Mater Sci. 52, 11834 (2017)

43. A. Pramothkumar, N. Senthilkumar, K. Jothivenkatachalam, Flake-like CuMnO$_2$ nanoparticles synthesized via co-precipitation method for photocatalytic activity. Physica B Condens Matter 572, 117 (2019)

44. A.D. Souza, M. Vagadia, M. Daivajna, Effect of nanoscale size reduction on the magnetic properties of Pr$_{0.6}$Sr$_{0.4}$MnO$_3$. J. Magn. Magn. Mater. 538, 168280 (2021)

45. A.D. Souza, S. Rayaprol, A. Sagdeo, A.K. Sinha, M. Daivajna, Magnetic phase transformation in La$_{0.7}$Bi$_{0.3}$MnO$_3$ (0.25 ≤ x ≤ 0.4). J. Magn. Magn. Mater. 511, 166966 (2020)

46. C. Kittel, Introduction to Solid State Physics (Wiley, New York, 1976)

47. A.K. Pramanik, A. Banerjee, Griffiths phase and its evolution with Mn-site disorder in the half-doped manganite Pr$_{0.5}$Sr$_{0.5}$MnO$_3$. J. Magn. Magn. Mater. 411909 (2020)

48. A.D. Souza, S. Rayaprol, M.S. Murari, M. Daivajna, Effect of Bi$_{3+}$ doping on charge ordering and high magnetic field phase diagram of Nd$_{0.65}$Bi$_{0.35}$MnO$_3$. J. Phys.: Condens. Matter 21, 195409 (2009)

49. C. Wang, Z.C. Xia, B. Zhao, D.W. Liu, Y.Q. Wang, Y.L. Su, Effects of Bi$_{3+}$ doping on charge ordering and high magnetic field phase diagram of Nd$_{0.65}$Bi$_{0.35}$MnO$_3$. Mater. Res. Bull. 121, 110611 (2020)

50. R. Seshadro, A. Nicola, Hill, Visualizing the role of Bi 6s “lone pairs” in the off-center distortion in ferromagnetic BiMnO$_3$. Chem. Mater. 13, 2892 (2001)

51. A.D. Souza, M.S. Murari, M.D. Daivajna, Structural, magnetic and magnetocaloric properties of Nanostructured La$_{0.7-x}$Bi$_x$Sr$_{0.3}$MnO$_3$ perovskites. Physica B Condens. Matter 580, 411909 (2020)

52. J.R. Sun, J. Gao, Y. Fei, R.W. Li, B.G. Shen, Doping effects on the phase separation in perovskite La$_{0.67-x}$Bi$_x$Ca$_{0.33}$MnO$_3$. Phys. Rev. B 67, 144414 (2003)

53. V. Markovich, R. Puzniak, I. Fita, A. Wisniewski, D. Mogilansky, A.K. Pramanik, A. Banerjee, Griffiths phase and its evo- lution, and Griffiths phase in Sm$_{0.1}$Ca$_{0.9}$MnO$_3$ nanoparticles. J. Phys.: Condens. Matter 12, 113912 (2020)
60. A.K. Pramanik, A. Banerjee, Finite-size effect on evolution of Griffiths phase in manganite nanoparticles. J. Phys. Condens. Matter 28, 35LT02 (2016)

61. J.A. Souza, J.J. Neumeier, Yu. Yi-Kuo, Magnetic signatures of ferromagnetic polarons in La$_{0.9}$Ca$_{0.1}$MnO$_3$: Colossal magnetoresistance is not a Griffiths singularity. Phys. Rev. B 78, 014436 (2008)

62. C.D. Batista, J. Eroles, M. Avignon, B. Alascio, Ferromagnetic polarons in manganites. Phys. Rev. B 62, 15047 (2000)

63. J.A. Souza, Yu. Yi-Kuo, J.J. Neumeier, H. Terashita, R.F. Jardim, Method for analyzing second-order phase transitions: Application to the ferromagnetic transition of a polaronic system. Phys. Rev. Lett. 94, 207209 (2005)

64. E. Rozenberg, M. Auslander, I.A. Shames, I. Felner, D. Mogilyansky, Y.M. Mukovskii, Griffith's phase versus chemical disorder in low-doped manganites: La$_{0.9}$Sr$_{0.1}$MnO$_3$ crystal revisited. J. Appl. Phys. 109, 07D902 (2011)

65. E. Rozenberg, M. Auslander, I. Felner, A.I. Shames, G. Gorodetsky, Y.M. Mukovskii, Thermodynamics of paramagnetic-ferromagnetic phase transition in La$_{1-x}$Ca$_{x}$MnO$_3$: “Griffiths singularity” versus Chemical Disorder and Lattice Effects. IEEE Tran. Magn. 46, 1299 (2010)

66. A. Shahee, K. Singh, R.J. Choudhary, N.P. Lalla, Evidence of ferromagnetic short-range correlations in cubic La$_{1-x}$Sr$_x$MnO$_3$: Evidence of ferromagnetic short-range correlations in cubic La$_{1-x}$Sr$_x$MnO$_3$. J. Alloys Compd. 509, 1373 (2011)

67. B. Roy, A. Poddar, S. Das, Electrical transport properties and magnetic cluster glass behavior of Nd$_{0.8}$Sr$_{0.2}$MnO$_3$ nanoparticles. I. Appl. Phys. 100, 104318 (2006)

68. B. Arun, M.V. Suneesha, M. Vasundhara, Comparative study of magnetic ordering and electrical transport in bulk and nano-grained Nd$_{0.8}$Sr$_{0.2}$MnO$_3$ manganites. J. Magn. Magn. Mater. 418, 265 (2016)

69. N.D. Sharma, S. Sharma, N. Choudhary, M.K. Verma, D. Singh, Comparative study of La$_{0.75}$Nd$_{0.05}$Ca$_{0.2}$MnO$_3$. J. Magn. Magn. Mater. 430, 13637 (2019)

70. B.D. Cullity, Introduction to Magnetic Materials (Addison-Wesley, MA, 1972)

71. A.D. Souza, P.D. Babu, S. Rayaprol, M.S. Murari, L.D. Mendonca, M. Daivajna, Size control on the magnetism of La$_{0.7}$Sr$_{0.3}$MnO$_3$. J. Alloys Compd. 797, 874 (2019)

72. E.C. Devi, I. Soibam, Law of Approach to Saturation in Mn–Zn Ferrite Nanoparticles. J. Supercond. Nov. Magn. 32, 1293 (2019)

73. D.H. Manh, P.T. Phong, T.D. Thanh, D.N.H. Nam, L.V. Hong, A.M. Tishin, Y.I. Spichkin, and Gd$_5$Ge$_2$Si$_2$ compounds as examples. J. Alloys Compd. 7351 (2017)

74. A. Elghoul, A. Krichene, N. Chniba Boudjada, W. Boujelben, Magnetic and magnetocaloric properties of La$_{0.75}$Bi$_{0.05}$Sr$_{0.2}$MnO$_3$. Appl. Phys. A 125, 780 (2019)

75. W. Mabrouki, A. Krichene, N.C. Boudjada, W. Boujelben, Sintering temperature effect on the magnetic properties of La$_{0.9}$Co$_{0.1}$MnO$_3$ manganite. Appl. Phys. A 126, 1 (2020)

76. H. Baaziz, A. Tozri, E. Dhahri, E.K. Hlil, Effect of particle size reduction on the structural, magnetic properties and the spin excitations in ferromagnetic insulator La$_{0.9}$Sr$_{0.1}$MnO$_3$ nanoparticles. Ceram. Int. 41, 2955 (2015)

77. M. Bourouina, A. Krichene, N.C. Boudjada, M. Khitouni, W. Boujelben, Structural, magnetic and magnetocaloric properties of nanostructured Pr$_{0.9}$Sr$_{0.1}$MnO$_3$ manganite synthesized by mechanical alloying. Ceram. Int. 43, 8139 (2017)

78. V.M. Andrade, R.J. Caraballo Vivas, S.S. Pedro, J.C.G. Tedesco, A.L. Rossi, A.A. Coelho, D.L. Rocco, M.S. Reis, Magnetic and magnetocaloric properties of La$_{0.66}$Ca$_{0.34}$MnO$_3$ tunable by particle size and dimensionality. Acta Mater. 102, 49 (2016)

79. T. Dipppong, O. Cadar, I.G. Deac, M. Lazar, G. Borodi, E.A. Leveli, Influence of ferrite to silica ratio and thermal treatment on porosity, surface, microstructure and magnetic properties of ZnO$_x$Ni$_{1-x}$Fe$_2$O$_4$/SiO$_2$ nanocomposites. J. Alloys Compd. 828, 154409 (2020)

80. T. Dipppong, E.A. Levei, I.G. Deac, F. Goga, O. Cadar, Investigation of structural and magnetic properties of Ni$_x$Zn$_{1-x}$Fe$_2$O$_4$ spinel ferrite nanoparticles synthesized by starch-assisted sol–gel auto combustion method and its ball milling. J. Magn. Magn. Mater. 378, 190 (2015)

81. A. Elghoul, A. Krichene, N. Chniba Boudjada, W. Boujelben, Magnetic properties and near-room-temperature large magnetocaloric effect in (La$_{1-x}$Bi$_x$)$_{0.3}$MnO$_3$ (0 ≤ x ≤ 1) spinel-based nanocomposites. J. Anal. Appl. Pyrolysis 144, 104713 (2019)

82. Q. Li, C.W. Kartikowati, S. Horie, T. Ogi, T. Iwaki, K. Okuyama, M. Tishin, Y.M. Mukovskii, Thermodynamic properties of nanostructured Pr$_{0.67}$Sr$_{0.33}$MnO$_3$ manganites. Appl. Phys. A 126, 1 (2020)

83. N. Nedelko, S. Lewinska, A. Pashchenko, I. Radelytskyi, R. Diduszko, E. Zubov, W. Lisowski et al., Magnetic properties and magnetocaloric effect in La$_{0.9}$Sr$_{0.1}$MnO$_3$ nanoparticles. J. Alloys Compd. 640, 433 (2015)

84. A. Kherrat, B. Jazia, E.K. Hilil, W. Boujelben, Bi doping effect on the critical behavior and magnetocaloric effect of Pr$_{0.8}$Bi$_{0.2}$MnO$_3$. J. Appl. Phys. 739, 101 (2018)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.