Tuning magnetic and magnetocaloric properties of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ through size modifications

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ABSTRACT

Particle size as an effective tool for controlling the magnetic and magnetocaloric properties of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ samples has been studied. In the present work, a direct influence of particle size on the magnitude of magnetization and magnetic transition temperature, T_C , can be seen. The T_C drops from 309 to 242 K, while the saturation magnetization (M_S) decreases from 3.6 to 0.5 $\mu_B/\text{f.u.}$ as the particle changes from 120 to 9 nm. Concurrently, coercivity (H_C) exhibits a drastic rise emphasizing the enhanced surface disorder in the nanoparticles. Another interesting observation is in the magnetic entropy change, ΔS , which though decreases in magnitude from 5.51 to 3.90 J/Kg-K as particle size decreases from 120 to 30 nm, but the temperature range of ΔS (i.e., relative cooling power, RCP) increases from 184.33 to 228.85 J/Kg. Such interplay between magnitude and wider temperature range of ΔS , which can be fine-tuned by particle size, provides an interesting tool for using surface spin disorder, as a control mechanism in modifying physical properties.

1 Introduction

Perovskites of the generic form, AMnO_3 (A = rare earth, transition or post-transition metal ion), are of interest for technological applications as well as for a basic understanding of the physical properties [1–3]. Alterations to the Mn–O–Mn bonds in AMnO_3 perovskite manganites result in dramatic changes of transport and magnetic properties, illustrating a strong interplay between the spin, charge, and lattice

degree of freedom. The MnO_6 octahedral environment in manganites could be modified through chemical substitutions at A - or Mn-sites, which mainly influence the charge density (i.e., a mixed-valence Mn state is created when A -site is substituted with monovalent or divalent ion) and induce lattice distortion [1–3]. The difference in the average ionic radii of A -site cations causes the variation in the Mn–O–Mn bond angles and Mn–O bond lengths thereby resulting in the tilting of MnO_6 octahedra. Compared to A -site, Mn-site substitution by a transition metal

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ion could introduce different magnetic interactions between Mn and substituted ion thereby driving the system from ferromagnetic (FM) to antiferromagnetic (AFM) state or vice-versa [1–3]. Apart from chemical substitution, particle size reduction to nanoscales has also been widely used to tune the physical properties of manganites [4, 5].

Recently, exploitation of the material properties at the nanoscale has gained wide importance due to their potential in medicine and industrial applications [6–8]. The significant advancement in the availability of strategies for the synthesis and characterization of the materials has resulted in the explosive growth of nanoscience and nanotechnology [9–14]. Nanosized materials such as nanotubes, nanowires, nanodiscs, and nanocomposites are widely used in logic circuits, magneto-electronic devices, optoelectronic devices, data storage, catalysis, electrochemistry, energy storage, drug delivery, and biotechnology [11–20] which are vital in the creation of future ultra-high-end technologies and devices. The spectral tuning in semiconductor quantum-confined nanomaterials, sensitizing dyes, and polymers allows the manipulation of optical bandgap over a broad range of solar spectrum to efficiently harvest solar energy in photovoltaics [20], while the large surface area and size, shape-dependent structural, electrical, and optical properties provide extensive usage in catalytic activities and water purification [11–14, 21, 22]. Additionally, the exponential growth in the field of nanomedicine and drug delivery has paved the way for the extensive use of nanomaterials for cancer treatment [23–25]. The large fraction of atoms residing on the surface of the nanoparticles is responsible for their distinguished properties compared to the bulk counterpart.

In magnetic nanoparticles, the enhanced surface to volume ratio exhibits interesting features such as low field magnetoresistance (MR), surface spin-glass behavior, super-paramagnetism, increased coercivity, and low field saturation magnetization, etc. [26–28] which are different from the bulk sample. These features make them suitable in biomedicine applications such as magnetic resonance imaging, magnetic hyperthermia, image-guided photothermal therapy etc., magnetic sensors, magnetic refrigeration, and magnetic chromatography [29–31]. Currently, the hunt for efficient materials with room temperature magnetocaloric properties has added momentum to the investigations on magnetic nanoparticles [30–32].

The feasibility of tuning the magnetic transitions spread over a broad temperature range with large magnetization and high chemical stability ensuring their potential as magnetocaloric material [30–33].

$\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (PSMO) is a room temperature ferromagnet ($T_C = 310$ K) exhibiting exceptional magnetocaloric, thermoelectric, and magnetoresistance properties and has the potential for application in room temperature regime [34–36]. The material also shows a structural transition, (T_s) at ≈ 89 K which is observed as a drop in magnetization within the FM state of the material [34–37]. This results in the coexistence of normal and inverse magnetic entropy change in the single matrix which is very interesting as magnetic cooling of the sample can be achieved through both adiabatic magnetization and demagnetization in different temperature regimes which in turn enables the extension of the active region for magnetic refrigeration [34].

In view of the extraordinary properties of PSMO, in the present study, an effort has been made to investigate the effect of particle size reduction on the structural, magnetic, and magnetocaloric properties of PSMO. Previously, we had studied the influence of particle size reduction on the magnetism of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) where we noticed a systematic decrease in the net magnetization with a decrease in particle size along with the appearance of Griffith's like singularity [38]. Even though both PSMO and LSMO are room temperature FM, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ belongs to the category of large bandwidth manganite exhibiting FM over wide doping concentration of Sr^{2+} , whereas $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$ is an intermediate bandwidth manganite showing FM over limited concentration of Sr^{2+} [1]. Another point to consider is that in the case of LSMO, A-site comprises of non-magnetic ions only, while in the case of PSMO, the magnetic ion is also present at the A-site. Therefore, it would be of interest to evaluate the observation made in the case of LSMO for another FM manganite such as PSMO.

2 Experimental details

$\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ (PSMO) nanoparticles were prepared in a two-step process by using the *top-down* approach [38–40]. The polycrystalline bulk sample prepared by solid-state reaction method [41] was subjected to high-energy ball milling to get the nanosized sample.

The detailed methodology has been described in our earlier papers [38–41]. In the present study, 10 mm tungsten carbide balls were used and the ball mass to sample mass ratio was maintained at 20:1. The milling time (t_m) was varied from 0 to 240 min and a small quantity of sample was taken out at the end of certain time intervals up to 240 min.

The crystal structure and phase purity of the prepared samples were determined from the room temperature X-ray diffraction measurements carried out on a Bruker D2 Phaser powder X-ray diffractometer in the 2θ range of 20° – 80° with a step size of 0.02° using Cu-K α as the radiation source. Magnetic measurements were carried out using Quantum Design Superconducting Quantum Interference Device (SQUID) Vibrating Sample Magnetometer (VSM) in magnetic fields up to ± 70 kOe and temperature down to 2 K.

3 Results and discussions

3.1 Structural studies

Figure 1a shows the room temperature X-ray diffractograms of all samples. The XRD patterns were refined by the Rietveld method using Fullprof program [42]. All the XRD patterns were indexed using the orthorhombic structure, with space group $Pnma$ [41]. As seen from Fig. 1, with an increase in t_m from 0 to 240 min, the XRD peaks show broadening describing the reduction in particle size (D) and inducement of microstrain (ε) in the lattice. Figure 1b shows the variation in the full width at half maxima (FWHM) of the (1 2 1), (0 4 2), and (2 0 2) diffraction peaks with ball milling. A significant elevation in the FWHM has been observed during the beginning of ball milling compared to higher t_m .

From the detailed Rietveld analysis [43], an estimation of particle size (D) and microstrain (ε) has been obtained. Inset in Fig. 1b shows the variation in the D and ε as a function of t_m . A substantial reduction in the D has been noticed in the initial stage of ball milling up to 90 min and thereafter the D appears to level off, while the ε manifests a monotonous increase up to 120 min of ball milling and then reaches a steady value. A similar variation in D and ε with t_m has been observed in case of $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ [44], $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [38], and Bi-doped $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ [39, 40]. The significant changes in the D and ε

during the commencing state of ball milling could be attributed to the enhanced rate of dislocation densities and defects induced due to the constant collision between the sample mass and balls with the walls of the vials [44–46]. Also, since the feed size at the beginning of ball milling is larger in dimension compared to after each t_m , the reduction in D and increment in ε are higher during the starting stage of ball milling as bigger particles are broken into smaller ones.

Thus, based on the estimated D from XRD analysis (inset in Fig. 2), four samples obtained after $t = 0, 20, 120$, and 240 min of ball milling having particle size $D = 120, 30, 11$, and 9 nm, respectively, were chosen for further investigation on the influence of particle size reduction on magnetization and magnetocaloric properties.

3.2 Magnetization studies

Figure 2 shows the dc magnetization plots for PSMO- D ($D = 120, 30, 11$, and 9 nm), in the temperature range of 2–380 K in an applied magnetic field of 100 Oe. The magnetization has been recorded under zero-field-cooled (ZFC) and field-cooled (FC) protocols. On lowering of temperature from 380 K, all samples undergo a paramagnetic (PM) to ferromagnetic (FM) transition at T_C , which decreases from 309 K for PSMO-120 to 246 K for PSMO-9 (Inset (a) in Fig. 2). In addition to this, a step-like drop in ZFC and FC curve has been observed at $T_S = 88$ K for PSMO-120 and PSMO-30 samples. This step-like feature is attributed to the orthorhombic (space group $Pnma$) to monoclinic (space group $I2/a$) structural transition in $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ [35, 37]. In the case of PSMO-11 and PSMO-9, the low-temperature drop in ZFC and FC curves is completely suppressed. However, the dM/dT plot (not shown here) exhibits a peak at 30 K for PSMO-11 and 27 K for PSMO-9, which could be assigned to the structural transition in the system. Also, with the decrease in D , the magnetic transition broadens. The width of dM/dT peak plotted as a function of D^{-1} (Inset (a) in Fig. 2), displays a systematic increase with a decrease in D probably due to the weak magnetic interaction among the spins on the surface of the nanoparticles. Further, in the FM phase, all the samples exhibit a large bifurcation in the ZFC and FC curves which indicates the presence of magnetic inhomogeneity (inset (b) in Fig. 2). The

Fig. 1 **a** Room temperature XRD patterns of bulk and ball-milled PSMO. Inset shows the Rietveld-refined XRD pattern for bulk PBSMO-0 sample. **b** A plot showing the variation in FWHM of (1 2 1), (0 4 2), and (2 0 2) diffraction peaks for bulk and ball-milled PSMO. Inset shows the variation of particle size and microstrain is shown as a function of milling time

strength of this bifurcation is measured by the M_{FC} – M_{ZFC} which is maximum for PSMO-30 sample.

With an increase in the magnitude of the external field from 0.1 to 50 kOe (Fig. 3a–c), the value of magnetization enhances significantly and T_C shifts toward the higher temperature. The increase in T_C with H implies the enhancement in the ferromagnetism as a higher magnetic field is expected to strengthen the exchange interaction between the parallel aligned magnetic spins thereby stabilizing the ferromagnetic state in the system. Also, the step noticed in the FC curve at T_S subdues with H and vanishes for $H = 50$ kOe for PSMO-120 and PSMO-30. Repaka et al. [34] using differential thermal analysis technique reported the nature of transition at T_S in PSMO to be first order. From neutron diffraction experiments, Ritter et al. [37] and Boujleben et al. [35] assigned the anomaly at T_S to the orthorhombic to monoclinic structural transition. Their refinement of neutron data showed the coexistence of two phases at the lowest temperature of 10 K indicating the incompleteness of structural transition.

To gain more insights into the magnetic state of the system, field-dependent magnetization loops were recorded on the prepared samples at different temperatures. Figure 4a shows the M–H loops for PSMO- D ($D = 120, 30, 11$, and 9 nm) samples at $T = 300$ K. The M–H curves are unsaturated with spontaneous

moment representing the features of weak ferromagnetic interaction among the spins as the samples are at the verge of PM to FM transitions, whereas at $T = 3$ K (Fig. 4b), the M–H loops indicate the ordered ferromagnetic state in the system. However, the net magnetization drops with a decrease in D , and the magnetization curves remain unsaturated for the nanoparticles compared to the bulk. The variation in the coercivity (H_C) plotted as a function of D (Fig. 5) shows a monotonous rise with a decrease in D probably due to the enhanced surface anisotropy in nanoparticles as size comes down [47]. Inset in Fig. 5 shows the H_C vs D^{-1} data fitted to the equation $H_C = m + n/D$, where m and n are constants. It may be noticed that H_C varies linearly with D^{-1} indicating the multidomain nature of the nanoparticles [47]. The increase in H_C can be accounted by the upsurge in the lattice strain induced due to the broken bonds which adds up to the surface anisotropy.

Figure 6 shows the temperature evolution of saturation magnetization (M_S). With a drop in temperature from 300 K, M_S displays an increment corroborating the transition in the system from PM to FM state. For ordered ferromagnets, at $T < T_C$ where spin fluctuations dominate the variation in M_S , temperature-dependent M_S could be accounted by the Bloch law given as [48, 49], $M_S = M_0(1 - BT^\alpha)$, where M_0 is the saturation magnetization at 0 K, B is the

Fig. 2 A plot of temperature-dependent *dc* magnetization for bulk and ball-milled PSMO in an applied field of 100 Oe. Inset **a** shows the variation in T_C and width of dM/dT as a function of D^{-1} . The line connecting the points is a guide to the eyes. Inset **b** shows temperature variation of $M_{FC} - M_{ZFC}$

constant related to exchange integral, and α is Bloch exponent. Generally, for bulk system α is estimated to be $3/2$ and is well obeyed. However, in nanoparticles, α shows a deviation from $3/2$ [50, 51]. Inset in Fig. 6 shows the Bloch law fit given to M_S vs T data for PSMO-120, PSMO-30, and PSMO-9. The fitting parameters are tabulated in Table 1. The value of α decreases from 1.48 to 0.76 as particle size drops from 120 to 9 nm. Mostly α is found to be higher than $3/2$ for nanoparticles [47, 51, 52], whereas a few studies report a drop in the magnitude of α with size reduction [53, 54] which has been understood as a consequence of size effects, surface spin disorder, and the nature of interaction among the nanoparticles.

Further using the law of approach to saturation (LAS) fit [38–40, 55] given to the demagnetization

Fig. 3 Temperature evolution of *dc* magnetization (FCW) in different applied magnetic field for **a** PSMO-120, **b** PSMO-30, and **c** PSMO-11

curves in the first quadrant (Supplementary file SI), an estimate of M_S , uniaxial magnetocrystalline anisotropy parameter (K) [56], and structural defects parameter (a/H) has been obtained. The LAS fit given to the M – H data at 3 K and the fitting parameters are described in the supplementary file (SI). The value of a/H increases with a decrease in D , specify the growth in the structural defects with size reduction, while K exhibits a decrease probably due to the disorder in the core of the nanoparticles [57]. Similar variation in a/H and K has been previously noticed in the case of LSMO manganites [38–40]. Additionally, a large drop in the magnitude of M_S from 3.6 to 0.5 $\mu_B/$

Fig. 4 Magnetization versus ramping field at **a** $T = 300\text{ K}$ and **b** $T = 3\text{ K}$ for bulk and ball-milled PSMO

f.u. has been noticed with a decrease in D (Fig. 7). M_S plotted as a function of D^{-1} (inset in Fig. 7) shows a linear variation specifying a strong impact of particle size on M_S of the sample.

3.3 Magnetocaloric studies

To evaluate the influence of particle size reduction on the magnetocaloric (MCE) properties, magnetic entropy change (ΔS) values were determined from the iso-field magnetization data using Maxwell's thermodynamic equations [32, 58],

$$\Delta S(T, H) = S_M(T, H) - S_M(T, 0) = \int_0^H \left(\frac{\partial M}{\partial T} \right)_H dH \quad (1)$$

Fig. 5 Variation in H_C as a function of D . Inset shows a plot of H_C vs D^{-1} . The solid line represents the linear fit

Generally, the ΔS values are determined indirectly from the magnetization isotherms recorded across the magnetic transitions and the specific heat measurements [32, 58]. However, some recent literature reports the estimation of ΔS from iso-field magnetization measurements [59, 60]. A close overlap in the estimation of ΔS from isothermal and iso-field magnetization validates the application of the latter approach to estimate the MCE [41, 42]. Additionally, it has been reported that across first-order magnetic transition, estimation of ΔS from magnetic isotherms can result in unrealistic values which can be corrected from iso-field magnetization [59, 60] measurements.

Figure 8a–c shows the evolution of ΔS as a function of temperature for PSMO- D ($D = 120, 30$ and 11 nm) under different magnetic fields. As expected, the magnitude of ΔS increases with an increase in the applied magnetic field and exhibits a maximum across T_C . For PSMO-120 and PSMO-30, ΔS manifests a negative maximum at T_C and a small positive

Fig. 6 Temperature evolution M_S for bulk and ball-milled PSMO. Inset shows the Bloch law fit (dashed lines) to M_S vs T . The data points for PSMO-9 in inset are multiplied by a factor 5

maximum at T_S , thereby representing both normal and inverse MCE in the same material. The observed characteristics match with the report of Repaka et al. [34]. The maximum entropy change, ΔS_M , recorded for $\Delta H = 50$ kOe, is -5.50 J/Kg-K at T_C and 0.35 J/Kg-K at T_S for PSMO-120. These values are in good agreement with the reported literature for bulk PSMO [34]. With a decrease in particle size, the

Fig. 7 A plot showing the variation of M_S as a function D . Inset shows the linear fit (solid line) given to M_S vs D^{-1}

magnitude of ΔS drops, and the peak broadens. The observed ΔS_M values are tabulated in table 2. A huge drop in the magnitude of ΔS has been noticed from 3.91 to 0.61 J/Kg-K for $\Delta H = 50$ kOe as D changes from 30 to 11 nm.

The relative cooling power (RCP) is defined as $RCP = \Delta S_M \times \delta T_{FWHM}$, where ΔS_M corresponds to the maximum entropy change and δT_{FWHM} is the full width half maximum of ΔS curve that reveals the suitability of the material for magnetic refrigeration

Table 1 Values of T_C , T_S , M_S , M_0 and other calculated microstructural parameters for bulk and ball-milled PSMO samples

Sample	PSMO-120	PSMO-30	PSMO-11	PSMO-9
T_C (K)	309	308	274	246
T_S (K)	88	88	30	31
M_S —3 K ($\mu_B/f.u.$)	3.820 ± 0.020	3.588 ± 0.014	1.036 ± 0.005	0.627 ± 0.0048
M_S —300 K ($\mu_B/f.u.$)	1.858 ± 0.011	1.435 ± 0.017	1.106 ± 0.003	0.0430 ± 0.001
M_0 ($\mu_B/f.u.$)	$3.82 (0.01)$	$3.56 (0.04)$	—	$3.82 (0.04)$
B (K°)	$6.12 (\pm 0.26) \times 10^{-5}$	$8.37 (\pm 0.13) \times 10^{-5}$	—	$8.35 (\pm 1.81) \times 10^{-3}$
α	$1.48 (\pm 0.08)$	$1.45 (\pm 0.03)$	—	$0.76 (\pm 0.04)$
Shell thickness (t) (nm)	—	0.99	2.34	2.40

Fig. 8 Variation in magnetic entropy change (ΔS) plotted as a function of temperature for **a** PSMO-120, **b** PSMO-30, and **c** PSMO-11

application. The values of ΔS_M , δT_{FWHM} , and RCP for different applied fields have been summarized in Table 2. With a decrease in D , ΔS_M drops while δT_{FWHM} shows a monotonous increase. RCP improves from 184.33 to 228.85 J/Kg as D decreases from 120 to 30 nm. For further decrease in D (i.e., $D = 11$ nm), RCP drops to 113.11 J/Kg. However, with an increase in the magnitude of the applied magnetic field, ΔS_M , δT_{FWHM} , and RCP values demonstrate a systematic increment (Table 2).

The large variation in ΔS across T_C could be accounted for by considering the change in magnetization and the spin lattice coupling across the magnetic ordering temperature [32]. The variation in

the Mn–O–Mn bond angle and Mn–O bond length with temperature results in the volume change, thereby influencing the ΔS values. A comparison of obtained values of ΔS from the present study with a few reported literature [61–71] is summarized in Table 3. The ΔS_M for bulk PSMO estimated from our samples is slightly higher compared to those reported by Zemni et al. [70] and Mamatha et al. [71] probably due to the different sample synthesis conditions. Even though compared to Gd and $\text{La}_{0.6}\text{Dy}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$, the observed ΔS_M in the present study seems smaller, but is comparable to other related systems.

In the light of the observed results, it is interesting to note that, the systematic reduction in the particle size directly influences the magnetization and MCE values. An abrupt drop in T_C , the magnitude of magnetization, and ΔS have been noticed as particle size reduces. The observed results could be explained by considering the core–shell model for the nanoparticles [72]. According to the core–shell model, each PSMO nanoparticle is made up of FM core having the same properties as that of the bulk of the material, while the shell is composed of broken bonds and randomly oriented magnetic spins. The shell thickness increases with a decrease in particle size. Assuming the net magnetization of the shell to be zero, an estimate of shell thickness (t) can be obtained from the relation [73],

$$t = \frac{D}{2} \left(1 - \left(\frac{M_{S(\text{Nano})}}{M_{S(\text{Bulk})}} \right)^{1/3} \right) \quad (2)$$

where D is the particle size, $M_{S(\text{Bulk})}$ and $M_{S(\text{Nano})}$ correspond 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^{-1} plot (inset in Fig. 7). The obtained values of shell thickness are tabulated in Table 1. Figure 9 shows a plot of the ratio of shell thickness to particle size (i.e., t/D) versus D . It can be observed that the t/D ratio exhibits a monotonous increase with particle size reduction. A linear variation in t/D as a function of D^{-1} implies a direct impact of size reduction on the thickness of non-magnetic shell which controls the properties of nanoparticles (Inset of Fig. 9). Similar variation in shell thickness with D has been noticed previously in case of doped LSMO nanoparticles [38–40]. Since ball milling induces more defects into the nanoparticle surface, a weak magnetic interaction among the spins on the surface of the nanoparticles results in the

Table 2 Values of ΔS_M , δT_{FWHM} , and RCP for different applied magnetic fields for bulk and ball-milled PSMO

Sample	ΔH (kOe)	ΔS_M (J/Kg K)	δT_{FWHM} (K)	RCP (J/Kg)
PSMO-120	1	0.18	8.9	1.60
	10	1.85	14.69	27.17
	50	5.51	33.48	184.47
PSMO-30	1	0.07	13.11	0.93
	10	1.03	25.25	26.21
	50	3.90	58.47	228.33
PSMO-11	1	0.0044	119.59	0.53
	10	0.10	150.15	16.19
	50	0.61	184.71	113.30

Table 3 A comparison of ΔS_M and RCP values for different samples

Compound	T_C (K)	ΔH (kOe)	ΔS_M (J/kg-K)	RCP (J/Kg)	Refs
Gd	295	50	10.2	410	[61]
La _{0.8} Sr _{0.2} MnO ₃	324	50	3.1	304	[62]
La _{0.6} Pr _{0.2} Sr _{0.2} MnO ₃	244	50	4.16	174.7	[63]
Pr _{0.55} Sr _{0.45} MnO ₃	300	30	1.71	143.64	[64]
Pr _{0.6} Sr _{0.3} Ag _{0.1} MnO ₃	287	30	1.74	—	[65]
La _{0.5} Eu _{0.2} Sr _{0.3} MnO ₃	292	50	4.46	203	[66]
La _{0.6} Nd _{0.1} (CaSr) _{0.3} Mn _{0.9} V _{0.1} O ₃	300	50	4.23	205.35	[67]
Pr _{0.6} Sr _{0.3} K _{0.1} MnO ₃	301	20	3.09	95.6	[68]
La _{0.6} Dy _{0.1} Sr _{0.3} MnO ₃	307	50	8.314	187	[69]
Pr _{0.6} Sr _{0.4} MnO ₃	321	25	2.3	35.5	[70]
Pr _{0.6} Sr _{0.4} MnO ₃	310	60	3.9	56	[71]
Pr _{0.6} Sr _{0.4} MnO ₃	310	50	4.65	182.5	[34]
Pr _{0.6} Sr _{0.4} MnO ₃ , $D = 120$ nm	309	50	5.51	184.47	Present work
Pr _{0.6} Sr _{0.4} MnO ₃ , $D = 30$ nm	308	50	3.90	228.33	Present work

broad magnetic transitions compared to bulk thereby resulting in large values of δT_{FWHM} . The increased separation between the ferromagnetic core of the nanoparticles leads to reduced magnetic interaction among the core which in turn shifts the T_C toward lower temperatures, hinders T_S with a reduction in the magnitude of M_S , and increases H_C .

Since for magnetic refrigeration application, an active magnetocaloric material requires large magnetic entropy, change values spread over a wide temperature range, one of the efficient ways to obtain materials with desired properties is material engineering. As it is well understood that the magnetization and magnetic transitions in manganites could be easily tuned by changing the stoichiometry, synthesis parameters, and particle size reduction [1, 4], from the present study, it can be noticed that PSMO- D ($D = 120, 30, 11$ nm) exhibits magnetic ordering in the vicinity of room temperature. With a drop in particle size, even though ΔS reduces, δT_{FWHM} increases and RCP values improve for $D = 30$ nm.

This indicates that ball milling can be used as an efficient tool to alter the properties of nanoparticles retaining the bulk characteristics.

4 Conclusions

In the present work, a systematic analysis of the XRD pattern and magnetization data has been carried out to understand the role of particle size reduction on the structural, magnetic, and magnetocaloric properties of PSMO manganite. As the milling time changes from 0 to 240 min, the particle size decreases from 120 to 9 nm. Correspondingly, T_C drops from 309 to 246 K and T_S hinders from 88 to 27 K with a drastic drop in the net magnetization, while coercivity (H_C) displays a monotonous increase. A deviation from Bloch's law observed for ball-milled nanoparticles demonstrates the enhanced surface disorder with particle size reduction. Even though the magnitude of ΔS decreases with size reduction

Fig. 9 Plot shows the variation in t/D as a function of D . Inset shows the linear fit given to t vs D^{-1}

from 5.51 to 3.91 J/Kg-K, the broadened magnetic transitions in nanoparticle improves the RCP of intermediate size sample (i.e., $D = 30$ nm) from 184.33 to 228.85 J/Kg. The observed direct relation between the magnetization and particle size could be explained considering the core-shell model for the nanoparticles. Such an interplay between the particle size and magnetic properties of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ is worth exploring as it manifests the use of surface disorder to control the magnetism in magnetic nanoparticles.

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Declarations

Conflict of interest The authors declare that there is no known conflict of interest regarding the publication of this manuscript.

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References

1. C.N. Rao, Bernard Raveau, *Colossal Magnetoresistance, Charge Ordering and Related Properties of Manganese Oxides* (World Scientific, Singapore, 1998).
2. T.A. Kaplan, S.D. Mahanti (eds.), *Physics of Manganite* (Springer, New York, 2006)

3. A.P. Ramirez, Colossal magnetoresistance. *J. Phys.* **39**, 8171–8199 (1997)
4. V. Markovich, A. Wisniewski, H. Szymczak, Magnetic properties of perovskite manganites and their modifications, in *Handbook of Magnetic Materials*, vol. 22 (Elsevier, 2014), pp. 1–201
5. T. Zhang, X.P. Wang, Q.F. Fang, X.G. Li, Magnetic and charge ordering in nanosized manganites. *Appl. Phys. Rev.* **1**, 031302 (2014)
6. C.N. Rao, A. Muller, A.K. Cheetham, *The Chemistry of Nanomaterials* (Wiley-Vch, Weinheim, 2005).
7. Y. Gogotsi (ed.), *Nanomaterials Handbook* (CRC Press, Boca Raton, 2017)
8. L. Cheng, C. Wang, L. Feng, K. Yang, Z. Liu, Functional nanomaterials for phototherapies of cancer. *Chem. Rev.* **114**, 10869–10939 (2014)
9. A.S. Edelstein, R.C. Cammarata (eds.), *Nanomaterials: Synthesis, Properties and Applications* (CRC Press, Boca Raton, 1998)
10. G. Cao, *Nanostructures & Nanomaterials: Synthesis, Properties & Applications* (Imperial College Press, London, 2004).
11. S. Zinatloo-Ajabshir, M.S. Morassaei, O. Amiri, M. Salavati-Niasari, Green synthesis of dysprosium stannate nanoparticles using *Ficus carica* extract as photocatalyst for the degradation of organic pollutants under visible irradiation. *Ceram. Int.* **46**, 6095–6107 (2020)
12. S. Zinatloo-Ajabshir, Z. Salehi, O. Amiri, M. Salavati-Niasari, Simple fabrication of $\text{Pr}_2\text{Ce}_2\text{O}_7$ nanostructures via a new and eco-friendly route; a potential electrochemical hydrogen storage material. *J. Alloys Compd.* **791**, 792–799 (2019)
13. S. Zinatloo-Ajabshir, M.S. Morassaei, O. Amiri, M. Salavati-Niasari, L.K. Foong, $\text{Nd}_2\text{Sn}_2\text{O}_7$ nanostructures: green synthesis and characterization using date palm extract, a potential electrochemical hydrogen storage material. *Ceram. Int.* **46**, 17186–17196 (2020)
14. S.A. Heidari-Asil, S. Zinatloo-Ajabshir, O. Amiri, M. Salavati-Niasari, Amino acid assisted-synthesis and characterization of magnetically retrievable $\text{ZnCo}_2\text{O}_4\text{--Co}_3\text{O}_4$ nanostructures as high activity visible-light-driven photocatalyst. *Int. J. Hydrogen Energy* **45**, 22761–22774 (2020)
15. R. Skomski, Nanomagnetism. *J. Phys.* **15**, R841–R846 (2003)
16. R.H. Kodama, Magnetic nanoparticles. *J. Magn. Magn. Mater.* **200**, 359–372 (1999)
17. G. Reiss, A. Hütten, Applications beyond data storage. *Nat. Mater.* **4**, 725–726 (2005)
18. S. Zinatloo-Ajabshir, N. Ghasemian, M. Mousavi-Kamazani, M. Salavati-Niasari, Effect of zirconia on improving NO_x reduction efficiency of $\text{Nd}_2\text{Zr}_2\text{O}_7$ nanostructure fabricated by a new, facile and green sonochemical approach. *Ultrason. Sonochem.* **71**, 105376 (2021)
19. S. Zinatloo-Ajabshir, M. Baladi, M. Salavati-Niasari, Enhanced visible-light-driven photocatalytic performance for degradation of organic contaminants using PbWO_4 nanostructure fabricated by a new, simple and green sonochemical approach. *Ultrason. Sonochem.* **72**, 105420 (2021)
20. G. Chen, J. Seo, C. Yang, P.N. Prasad, Nanochemistry and nanomaterials for photovoltaics. *Chem. Soc. Rev.* **42**, 8304–8338 (2013)
21. M.S. Morassaei, S. Zinatloo-Ajabshir, M. Salavati-Niasari, Simple salt-assisted combustion synthesis of $\text{Nd}_2\text{Sn}_2\text{O}_7\text{--SnO}_2$ nanocomposites with different amino acids as fuel: an efficient photocatalyst for the degradation of methyl orange dye. *J. Mater. Sci.* **27**, 11698–11706 (2016)
22. M. Mousavi-Kamazani, S. Zinatloo-Ajabshir, M. Ghodrati, One-step sonochemical synthesis of $\text{Zn(OH)}_2/\text{ZnV}_3\text{O}_8$ nanostructures as a potent material in electrochemical hydrogen storage. *J. Mater. Sci.* **31**, 17332–17338 (2020)
23. A.J. Hubbell, A. Chilkoti, Nanomaterials for drug delivery. *Science* **337**, 303–305 (2012)
24. A. Tiwari, A. Tiwari (eds.), *Nanomaterials in Drug Delivery, Imaging, and Tissue Engineering* (Wiley, Scrivener, 2013)
25. K.H. Bae, H.J. Chung, T.G. Park, Nanomaterials for cancer therapy and imaging. *Mol. Cells* **31**, 295–302 (2011)
26. S.P. Gubin (ed.), *Magnetic Nanoparticles* (Wiley, New Year, 2009)
27. A.E. Berkowitz, R.H. Kodama, S.A. Makhlof, F.T. Parker, F.E. Spada, E.J. McNiff Jr, S. Foner, Anomalous properties of magnetic nanoparticles, *J. Magn. Magn. Mater.* **196**, 591–594 (1999)
28. S. Bedanta, K. Wolfgang, Supermagnetism. *J. Phys. D.* **42**, 013001 (2008)
29. V.K. Varadan, L. Chen, J. Xie, Nanomedicine: design and applications of magnetic nanomaterials, nanosensors and nanosystems, John Wiley & Sons, 2008
30. Y. Wang, J. Shao, Y. Yu, Q. Shi, Y. Zhu, T. Miao, H. Lin, L. Xiang, Q. Li, P. Cai, W. Wang, Enhanced magnetocaloric effect in manganite nanodisks. *Phys. Rev. Mater.* **3**, 084411 (2019)
31. A. Biswas, S. Chandra, H. Srikanth, Magnetocaloric properties of nanocrystalline LaMnO_3 : enhancement of refrigerant capacity and relative cooling power. *J. Alloys Compd.* **545**, 157–161 (2012)
32. M.H. Phan, S.C. Yu, Review of the magnetocaloric effect in manganite materials. *J. Magn. Magn. Mater.* **308**, 325–340 (2007)
33. N.S. Bingham, M.H. Phan, H. Srikanth, M.A. Torija, C. Leighton, Magnetocaloric effect and refrigerant capacity in

- charge-ordered manganites. *J. Appl. Phys.* **106**, 023909 (2009)
34. D.V. Maheswar Repaka, T.S. Tripathi, M. Aparnadevi, R. Mahendiran, Magnetocaloric effect and magnetothermopower in the room temperature ferromagnet $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. *J. Appl. Phys.* **112**, 123915 (2012)
  35. W. Boujelben, M. Ellouze, A. Cheikh-Rouhou, J. Pierre, Q. Cai, W.B. Yelon, K. Shimizu, C. Dubourdieu, Neutron diffraction, NMR and magneto-transport properties in the $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ perovskite manganite. *J. Alloys Compd.* **334**, 1–8 (2002)
  36. A. Chanda, R. Mahendiran, Effects of external magnetic field and hydrostatic pressure on magnetic and structural phase transitions in $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. *J. Appl. Phys.* **124**, 043902 (2018)
  37. C. Ritter, P.G. Radaelli, M.R. Lees, J. Baratt, G. Balakrishnan, Mc.K. Paul, A new monoclinic perovskite allotype in $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. *J. Solid State Chem.* **127**, 276–282 (1996)
  38. A.D. Souza, P.D. Babu, S. Rayaprol, M.S. Murari, L.D. Mendonca, M. Daivajna, Size control on the magnetism of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. *J. Alloy Compd.* **797**, 874–882 (2019)
  39. A.D. Souza, P.D. Babu, S. Rayaprol, M.S. Murari, M. Daivajna, Study of combined effect of partial Bi doping and particle size reduction on magnetism of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$. *J. Magn. Magn. Mater.* **497**, 166020 (2020)
  40. A.D. Souza, M.S. Murari, M. Daivajna, Structural, magnetic and magnetocaloric properties of nanostructured $\text{La}_{0.5}\text{Bi}_{0.2}\text{Sr}_{0.3}\text{MnO}_3$ perovskites. *Physica B* **580**, 411909 (2020)
  41. A.D. Souza, M. Vagadia, M. Daivajna, Short range ferromagnetic correlations above the curie temperature of $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ nanoparticles (under Review).
  42. T. Roisnel, J. Rodríguez-Carvajal, WinPLOTR: a windows tool for powder diffraction pattern analysis. *Mater. Sci. Forum* **378**, 118–123 (2001)
  43. J. Rodríguez-Carvajal, T. Roisnel, Line broadening analysis using FullProf*: determination of microstructural properties. *Mater. Sci. Forum* **443**, 123–126 (2004)
  44. S. Roy, I. Dubenko, D.D. Edorh, N. Ali, Size induced variations in structural and magnetic properties of double exchange $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 - \delta$ nano-ferromagnet. *J. Appl. Phys.* **96**, 1202 (2004)
  45. M. Sopicka-Lizer (ed.), *High-Energy Ball Milling: Mechanochemical Processing of Nanopowders* (Elsevier, Amsterdam, 2010)
  46. 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**, 11834–11850 (2017)
  47. B.D. Cullity, *Introduction to Magnetic Materials* (Addison-Wesley, Reading, MA, 1972)
  48. P.V. Hendriksen, S. Linderoth, P.-A. Lindgard, Magnetic properties of Heisenberg clusters, *J. Phys.* **5**, 5675 (1993)
  49. H. Kaplan, Harvey, A spin-wave treatment of the saturation magnetization of ferrites. *Phys. Rev.* **86**, 121 (1952)
  50. P.V. Hendriksen, Søren Linderoth, P.-A. Lindgård, Finite-size effects in the magnetic properties of ferromagnetic clusters, *J. Magn. Magn. Mater.* **104**, 1577–1579 (1992)
  51. J.P. Chen, C.M. Sorensen, K.J. Klabunde, G.C. Hadjipanayis, E. Devlin, A. Kostikas, Size-dependent magnetic properties of MnFe_2O_4 fine particles synthesized by coprecipitation. *Phys. Rev. B* **54**, 9288 (1996)
  52. N.C. Thuan, P.T. Phong, N.X. Phuc, Magnetic properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanoparticles prepared by reactive milling. *J. Alloys Compd.* **479**, 828–831 (2009)
  53. D. Zhang, K.J. Klabunde, C.M. Sorensen, G.C. Hadjipanayis, Magnetization temperature dependence in iron nanoparticles. *Phys. Rev. B* **58**, 14167 (1998)
  54. G. Xiong, Z. Mai, M. Xu, S. Cui, Y. Ni, Z. Zhao, X. Wang, L. Lu, Preparation and magnetic properties of CoCrFeO_4 nanocrystals. *Chem. Mater.* **13**, 1943–1945 (2001)
  55. E.C. Devi, I. Soibam, Law of approach to saturation in Mn–Zn ferrite nanoparticles. *J. Supercond. Nov. Magn.* **32**, 1293 (2018)
  56. D.H. Manh, P.T. Phong, T.D. Thanh, D.N.H. Nam, L.V. Hong, N.X. Phuc, Size effects and interactions in $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ nanoparticles. *J. Alloys Compd.* **509**, 1373 (2011)
  57. M. Thakur, K. De, S. Giri, S. Si, A. Kotal, T.K. Mandal, Interparticle interaction and size effect in polymer coated magnetite nanoparticles. *J. Phys.* **18**, 9093 (2006)
  58. A.M. Tishin, Y.I. Spichkin, *The Magnetocaloric Effect and Its Applications* (CRC Press, Boca Raton, 2016).
  59. H.N. Bez, H. Yibole, A. Pathak, Y. Mudryk, V.K. Pecharsky, Best practices in evaluation of the magnetocaloric effect from bulk magnetization measurements. *J. Magn. Magn. Mater.* **458**, 301–309 (2018)
  60. A. Magnus, G. Carvalho, A.A. Coelho, P.J. Von Ranke, C.S. Alves, The isothermal variation of the entropy (ΔS_T) may be miscalculated from magnetization isotherms in some cases: MnAs and $\text{Gd}_3\text{Ge}_2\text{Si}_2$ compounds as examples. *J. Alloys Compd.* **509**, 3452–3456 (2011)
  61. K.A. Gschneidner Jr., V.K. Pecharsky, A.O. Tsokol, Recent developments in magnetocaloric materials. *Rep. Prog. Phys.* **68**, 1479 (2005)
  62. M.E. Amano, I. Betancourt, J.L. Sánchez Llamazares, L. Huerta, C.F. Sánchez-Valdés, Mixed-valence $\text{La}_{0.80}(\text{Ag}_{1-x}\text{Sr}_x)_{0.20}\text{MnO}_3$ manganites with magnetocaloric effect. *J. Mater. Sci.* **49**, 633–641 (2014)

63. M. Zarifi, P. Kameli, M. Mansouri, H. Ahmadvand, H. Salamati, Magnetocaloric effect and critical behavior in $\text{La}_{0.8-x}\text{Pr}_x\text{Sr}_{0.2}\text{MnO}_3$ ($x = 0.2, 0.4, 0.5$) manganites. *Solid State Commun.* **262**, 20–28 (2017)
64. J. Fan, L. Pi, L. Zhang, W. Tong, L. Ling, B. Hong, Y. Shi, W. Zhang, Di Lu, Y. Zhang, Magnetic and magnetocaloric properties of perovskite manganite $\text{Pr}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$. *Physica B* **406**, 2289–2292 (2011)
65. D. Szewczyk, R. Thaljaoui, J. Mucha, P. Stachowiak, P. Vanderbenden, Specific heat and magnetocaloric effect in $\text{Pr}_{0.6}\text{Sr}_{0.4-x}\text{Ag}_x\text{MnO}_3$ manganites. *Intermetallics* **102**, 88–93 (2018)
66. S. Vadnala, S. Asthana, Magnetocaloric effect and critical field analysis in Eu substituted $\text{La}_{0.7-x}\text{Eu}_x\text{Sr}_{0.3}\text{MnO}_3$ ($x = 0.0, 0.1, 0.2, 0.3$) manganites. *J. Magn. Magn. Mater.* **446**, 68–79 (2018)
67. A. Dhahri, F.I.H. Rhouma, S. Mnefgui, J. Dhahri, E.K. Hlil, Room temperature critical behavior and magnetocaloric properties of $\text{La}_{0.6}\text{Nd}_{0.1}(\text{CaSr})_{0.3}\text{Mn}_{0.9}\text{V}_{0.1}\text{O}_3$. *Ceram. Int.* **40**, 459–464 (2014)
68. R. Thaljaoui, W. Boujelben, M. Pekała, K. Pekała, J.-F. Fagnard, M. Philippe Vanderbenden, Donten, A. Cheikhrouhou, Magnetocaloric effect of monovalent K doped manganites $\text{Pr}_{0.6}\text{Sr}_{0.4-x}\text{K}_x\text{MnO}_3$ ($x = 0$ to 0.2). *J. Magn. Magn. Mater.* **352**, 6–12 (2014)
69. L. Xu, L. Chen, J.F.K. Bärner, L. Zhang, Y. Zhu, L. Pi, Y. Zhang, D. Shi, Room-temperature large magnetocaloric effect and critical behavior in $\text{La}_{0.6}\text{Dy}_{0.1}\text{Sr}_{0.3}\text{MnO}_3$. *Ceram. Int.* **42**, 8234–8239 (2016)
70. S. Zemni, M. Baazaoui, J. Dhahri, H. Vincent, M. Oumezzine, Above room temperature magnetocaloric effect in perovskite $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$. *Mater. Lett.* **63**, 489–491 (2009)
71. M.D. Daivajna, A. Rao, Magnetocaloric effect in pristine and Bi-doped $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ manganite. *Solid State Commun.* **245**, 65–69 (2016)
72. M.A. Lopez-Quintela, L.E. Hueso, J. Rivas, F. Rivadulla, Intergranular magnetoresistance in nanomanganites. *Nanotechnology* **14**, 212 (2003)
73. T.A. Ho, T.D. Thanh, S. Oh, S.C. Yu, Effect of crystallite size on the thickness of nonmagnetic shell and magnetic properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. *J. Supercond. Nov. Magn.* **28**, 891 (2015)

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