1. Introduction

Magnetic properties of mixed valence perovskite manganites $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ ($\text{R}=$ La, Gd, Pr, Nd, Sm etc and $\text{A}=$ Sr, Ba and Ca) at the nanometer scale are currently the focus of intense investigations due to their interesting physical properties as well as potential technological applications [1–3]. Along with a wide range of functional properties like colossal magnetoresistance, magnetocaloric effect, the perovskite class of manganites also exhibit multiferroic [4, 5] properties which is technologically very important. Therefore, the past decade has seen an increased interest in the study of multiferroic perovskites [4, 6]. A spontaneous electric polarization in the presence of magnetic fields was reported in Gd$_{1-x}$Sr$_x$MnO$_3$ perovskite manganites [7]. When the size of magnetic particles is reduced to a few tens of nanometers, they exhibit fascinating magnetic and electronic properties that are significantly different from their bulk counterparts [1, 8–10]. In these manganese systems, novel magnetic properties such as colossal magnetoresistance [11] can be obtained around the ferromagnetic to paramagnetic transition temperature ($T_c$) [12]. However, the transition temperatures, i.e. the particle size dependent $T_c$ values for the same material system were found to vary in different investigations [12–14]. The conflicting results might be due to the influence of the fabrication process as well as different oxygen content of manganites [1]. It is reported that the $T_c$ values of the samples can be decreased by adopting different fabrication techniques for the preparation of
manganese nanoparticles due to very small variations in the chemical composition and oxygen stoichiometry [2]. It is also reported that in magnetic materials, the magnetic order in the surface of the particles is modified by forming a magnetically dead layer [2, 15, 16], and consequently affect the magnetization, transition temperature and anisotropy of the material system [2]. By using the available wet chemical methods, it is difficult to control the complex solution processes and the size of the synthesized nanoparticles [17]. Therefore, the synthesis of manganese nanoparticles with controlled size, chemical composition, oxygen stoichiometry and unmodified surface is of fundamental and technological interests.

The perovskite manganese nanoparticles of various compositions have been synthesized using the ball milling technique [14, 18–21] to produce nanoparticles from a few to tens nanometers [14]. However, the magnetic properties of the finer particles were found to degrade. The degradation was ascribed to the increase of the defect density and surface roughness of La0.8Sr0.2MnO3–δ nanoparticles due to the high energy ball milling [18]. During the fabrication of La0.62Sr0.33MnO3, manganese particles using ball milling, for a milling time longer than 40 h, the perovskite structure disappeared and a completely amorphous phase was formed [19]. Moreover, the magnetic measurements showed that ball milled samples had an inhomogeneous magnetic state [19].

Notably, the utilization of ultrasonic energy in a process called sonofragmentation offers a facile, versatile synthetic tool for the preparation of nanostructured materials that is often difficult by conventional methods [22–25]. Ultrasonic dispersion has extensive use to disperse sub-micron agglomerated powders in liquid suspensions. It is possible to break down the aggregates of nanocrystalline particles by using the effects of ultrasound which generates many localized hot spots with the particles within the solution [26] and during the process, the implosive collapse of the bubbles causes an inward rush of liquid known as shockwaves and microsteam in which high velocity is produced. Thus the agglomerates can be broken down utilizing the effects of ultrasound [27], resulting in reduction of particle size. Recently, we have synthesized Bi based Bi0.9Gd0.1Fe1–xTiO3 nanoparticles by ultrasonication of their micro-meter sized multiferroic bulk powder materials [22] with particle size that can be varied as a function of sonication time. Transmission electron microscopy imaging confirmed the formation of ultrasonically prepared single crystalline nanoparticles with a mean size of 11–13 nm for 60 min sonication.

In the present investigation, we have synthesized nanoparticles of rare-earth based Gd0.7Sr0.3MnO3 by ultrasonication of their bulk powder materials. For comparison, we have also synthesized Gd0.7Sr0.3MnO3 nanoparticles by planetary ball milling. This compound was chosen due to the fact that Gd0.7Sr0.3MnO3 contain significant amount of heavy rare earth Gd and the magnetic properties of rare-earth based manganites are quite different from that of Bi based materials as reported elsewhere [28, 29]. The magnetic properties of Bi based manganites are attributed to the presence of highly polarizable 6s2 lone pair of electrons present on the Bi atom, which strongly decreases the mobility of εg electrons [28, 29]. Whereas the magnetic properties of rare earth based mixed valence perovskite manganites involve simultaneous transfer of an itinerant εg electron from the Mn3+ to the oxygen and from the oxygen to the neighbouring Mn4+ [30]. Moreover, in these manganite systems the conversion of Mn3+ to Mn4+ is significantly influenced by oxygen vacancies [31]. Till now, the perovskite Gd–Sr manganites [32] have been well studied in the bulk form as a single crystal [33] and polycrystalline samples [11]. However, due to the limitation of preparation techniques that allow reproducible fabrication of high crystalline nanoparticles of complex rare-earth based perovskite Gd0.7Sr0.3MnO3 manganites, many of the novel properties of these nanostructures are yet to be unveiled. Therefore, in this investigation, rare-earth based Gd0.7Sr0.3MnO3 nanoparticles were produced by ultrasonication as well as conventional ball milling techniques. The structural and magnetic properties of the synthesized nanoparticles were investigated and compared to their corresponding bulk materials.

2. Experimental details

The perovskite manganite with nominal composition Gd0.7Sr0.3MnO3 was prepared initially by conventional solid state reaction technique which was described in details elsewhere [34, 35]. The analytical grade Gd2O3, SrCO3 and MnCO3 powders were mixed and ground in an agate mortar till a homogeneous mixture was formed. This mixture was calcined at around 1100 °C for 18 h in a programmable furnace with intermediate grinding after 12 h. The powders were pressed into pellets of thickness 1 mm and diameter 10 mm by using a hydraulic press and sintered at 1300 °C for 6 h [34]. The sintered powder and pellets were used to measure the required structural, morphological and magnetic properties of the bulk materials. In order to prepare the nanoparticles by using ultrasonication and ball milling techniques, the ceramic pellets were ground again into powder by manual grinding to obtain powder materials.

A portion of the micro-meter size powder was subsequently mixed with isopropanol. The mixtures of isopropanol and powder with a mass percentage of ~0.5 % were put into an ultrasonic bath (power 50 W) and sonicated for 60 min. After six hours rest, ~30% of the mass was collected as supernatant from the mixture and dried naturally for the required characterization. Another portion of the powder materials was used to prepare nanoparticles of Gd0.7Sr0.3MnO3 manganites by using ball milling technique as was described in the published reports [14, 18]. The bulk polycrystalline Gd0.7Sr0.3MnO3 powder was ball milled for 4–12 h by conventional planetary ball mill.
(MTI corporation, Model: QM-3SP2) with stainless steel vials and zirconia balls. The ratio of the ball and powder weight was 50:1 and the rotating speed was set to 300 rpm. The preparation of Gd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) nanoparticles by using ultrasonication and ball milling techniques is illustrated schematically in figure 1.

The crystal structures of the bulk powder materials, nanoparticles prepared by ultrasonication and also prepared by ball milling were determined from x-ray diffraction (XRD) data. XRD patterns were collected at room temperature using a diffractometer (Rigaku SmartLab) with CuK\(_\alpha\) radiation. Rietveld analysis of XRD data was carried out using the FULLPROF package [36]. The microstructure of the surface of the sintered pellets, and the size and distribution of the synthesized nanoparticles were observed using a field emission scanning electron microscope (FESEM, JEOL, JSM 5800). X-ray photoelectron spectroscopy (XPS, ULVAC-PHI Inc., Model 1600) analysis was carried out with a Mg-K\(_\alpha\) radiation source. The temperature dependent magnetization measurements of Gd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) bulk materials and nanoparticles were carried out using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-XL7, USA) both at zero field cooling (ZFC) and field cooling (FC) processes. The field dependent magnetization measurements were also carried out using the same SQUID magnetometer at 20 K and 300 K.

3. Results and discussions

3.1. Structural analysis

The measured and calculated XRD intensity patterns after Rietveld refinement of Gd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) bulk materials, and nanoparticles prepared by ultrasonication and ball milling techniques for 4 h, 8 h and 12 h milling time are shown in figures 2(a)–(e) respectively. The Bragg positions of the reflections of Gd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) and other oxides are indicated by vertical lines below the pattern. The lattice parameters and cell volumes of bulk materials and nanoparticles prepared by ultrasonication and ball milling techniques are presented in table 1. The structure of Gd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) manganites is an orthorhombically distorted perovskite structure (spatial group Pbnm) determined by Rietveld refinement and is in agreement with the structure observed in related compounds [11, 32]. The lattice parameters for the bulk polycrystalline sample are: \(a = 5.399 (4) \text{ Å}, b = 5.472 (1) \text{ Å}\) and \(c = 7.625 (1) \text{ Å}\). The lattice parameters are: \(a = 5.399 (1) \text{ Å}, b = 5.478 (1) \text{ Å}\) and \(c = 7.607 (1) \text{ Å}\) for the corresponding nanoparticles prepared by ultrasonication. The lattice parameters are in good agreement with the reported parameters of orthorhombic Gd\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) [11] manganites. In order to quantitatively express the microscopic distortion relative to the ideal perovskite structure, orthorhombic deformation (D\%) defined as

\[
D = \frac{1}{2} \sum_{i=1}^{3} \left| \frac{a_i - \bar{a}}{a_i} \right| \times 100
\]

(1)

where \(a_1 = a, a_2 = b, a_3 = c/\sqrt{2}\), and \(\bar{a} = (abc/\sqrt{2})^{1/3}\) [37], have also been calculated and inserted in table 1. The D\% was nominally changed for ultrasonically prepared and 4 h ball milled nanoparticles. However, for milling time higher than 8 h, D\% has increased significantly.

XRD analysis is one of the common ways to investigate the nature of crystalline and amorphous phases of a material [38]. The peaks intensity of the ultrasonically prepared nanoparticles slightly decrease together with a little broadening of the peaks, which indicate a decrease in crystallinity of the nanoparticles. On the contrary, the intensity peaks of the ball milled particles decrease drastically with milling time along with a large broadening.

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Figure 1. A scheme delineating the preparation of Gd\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) nanoparticles by using ultrasonication and ball milling techniques.
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of the peaks as shown in figures 2(c)–(e). This indicates a notable reduction in the crystallinity of the materials due to ball milling [39]. The width of the (200) peak of the bulk materials is 0.383, which was increased to 0.532 for ultrasonically prepared nanoparticles. The width of the same peaks for ball milling nanoparticles gradually increase with prolongation of the milling time. Table 2 shows the values of the FWHM of (200) peaks for all materials under scrutiny. While performing this calculation, instrumental peak broadening factor has been taken into consideration. To determine the instrumental broadening, a diffraction profile from a standard material like silicon has been collected as a reference. In previous investigations [40, 41], the instrumental broadening was corrected, corresponding to the peaks of the sample using the relation:

$$\beta = \sqrt{\beta_{\text{exp}}^2 - \beta_{\text{inst}}^2}$$

(2)

where, $\beta$, $\beta_{\text{exp}}$ and $\beta_{\text{inst}}$ are the FWHMs of the intrinsic profile, the experimental profile and the instrumental broadening profile respectively at the same value of $\theta$. In fact, the FWHMs of the obtained XRD peaks from the XRD machine are not simply the summation of the actual FWHM and FWHM of the reference. Rather the obtained response is the convoluted result of the desired intrinsic sample profile along with the instrumental broadening profile [42, 43]. Therefore, instead of simplified subtraction, using deconvolution operation, the effect of instrumental peak broadening has been minimized, and corrected FWHM of the (200) peaks of the samples were inserted in table 2. By using a block diagram the deconvolution operation system has been described.
It is noteworthy that lattice strain, which is a measure of the distribution of lattice constants arising from crystal imperfections and distortions, also affect the broadening of Bragg peak. Therefore, the microstrain of the synthesized samples was calculated using Williamson–Hall analysis [44] and the values are inserted in table 2. Like orthorhombic deformation, the microstrain was also found to increase gradually with milling time [45] and for 12 h ball milling sample the microstrain is significantly higher.

The broad and diffuse peaks particularly centered at 33° figures 2(b)–(e)) is a clear indication of crystalline to amorphous like phase transition of the bulk powder materials after sonication as well as ball milling. In a previous investigation, the intensity of peaks belonging to La0.67Sr0.33MnO3 manganites was also found to decrease gradually for a milling time >12 h [19]. The decrease in intensity of peaks suggested the appearance of an amorphous phase in La0.67Sr0.33MnO3 manganites when the milling time is longer than 12 h [19]. Notably, although XRD patterns provide indication of the formation of crystalline to amorphous like phase, however, the quantification of the amount of crystalline and amorphous phases is difficult [46]. In this investigation, using the Rietveld refinement procedure, the quantity of amorphous and crystalline phases of the synthesized samples have been calculated. Amorphousity has been calculated by the intensity ratio of the diffraction peaks and sum of all measured intensity with the help of X’Pert HighScore Plus where the program has been calibrated to the crystallinity analysis for a

| Samples | a_{orth} (Å) | b_{orth} (Å) | c_{orth} (Å) | Unit cell Volume (Å$^3$) | Orthorhombic Deformation D (%) | Fitting Parameters |
|---------|--------------|--------------|--------------|--------------------------|-------------------------------|--------------------|
| Bulk    | 5.399 (4)    | 5.472 (1)    | 7.625 (1)    | 225.3 (1)                | 0.63                          | $\chi^2 = 6.95$    |
|         |              |              |              |                          |                               | $R_p = 6.62$       |
|         |              |              |              |                          |                               | $R_f = 3.81$       |
|         |              |              |              |                          |                               | $\chi^2 = 3.54$    |
| Nano   | 5.399 (1)    | 5.478 (1)    | 7.607 (1)    | 225 (1)                  | 0.73                          | $R_p = 3.62$       |
|         |              |              |              |                          |                               | $R_f = 3.25$       |
|         |              |              |              |                          |                               | $\chi^2 = 5.62$    |
| 4 h    | 5.382 (2)    | 5.462 (2)    | 7.589 (3)    | 223.1 (1)                | 0.72                          | $R_p = 6.90$       |
|         |              |              |              |                          |                               | $R_f = 3.76$       |
|         |              |              |              |                          |                               | $\chi^2 = 5.42$    |
| 8 h    | 5.373 (2)    | 5.472 (2)    | 7.607 (4)    | 223.6 (1)                | 0.79                          | $R_p = 3.67$       |
|         |              |              |              |                          |                               | $R_f = 2.52$       |
|         |              |              |              |                          |                               | $\chi^2 = 6.53$    |
| 12 h   | 5.393 (3)    | 5.616 (2)    | 7.565 (4)    | 229.6 (2)                | 1.99                          | $R_p = 2.93$       |
|         |              |              |              |                          |                               | $R_f = 9.24$       |

Table 2. Wt% of the phases present in Gd0.7Sr0.3MnO3 samples estimated from the X’Pert HighScore Plus and Rietveld analysis. The table also shows various R factors such as $R_p$ (profile factor), $R_{wp}$ (weighted profile factor) and Gof (goodness-of-fit).

| Phases | Bulk (100%) | Nano (100%) | 4 h (100%) | 8 h (100%) | 12 h (100%) |
|--------|-------------|-------------|------------|------------|-------------|
| FWHM   | 0.383 | 0.532 | 0.775 | 0.905 | 0.964 |
| Microstrain % | 0.0242 (4) | 0.0408 (7) | 0.0833 (1) | 0.0975 (4) | 0.1176 (2) |
| Amorphousity | 12.4 (6) | 13.6 (1) | 14.9 (6) | 32.3 (5) | 35.9 (9) |
| Wt% GdSrMnO3 Orthorombic (pbnm) | 84.6 (6) | 83.2 (5) | 78.1 (8) | 61.7 (4) | 61.9 (4) |
| Wt% Mn2O3 Cubic (La3) | 0 | 0 | 5.2 (8) | 1.0 | 0.3 |
| Wt% SrO2 Tetragonal (I4 mmm$^{-1}$) | 3.0 | 2.9 | 1.4 (1) | 0.1 | 0.1 |
| Wt% Gd2O3 Cubic (La3) | 0.1 | 0.1 | 0.4 | 4 (2) | 1.8 (1) |
| $R_p$ (%) | 18.2 | 17.3 | 22.9 | 21.0 | 17.5 |
| $R_{wp}$ (%) | 11.6 | 10.8 | 16.3 | 17.0 | 15.2 |
| Gof (%) | 2.63 | 1.88 | 2.37 | 2.32 | 2.55 |

in supplemental information (stacks.iop.org/MRX/4/075012/mmedia)6. It is noteworthy that lattice strain, which is a measure of the distribution of lattice constants arising from crystal imperfections and distortions, also affect the broadening of Bragg peak. Therefore, the microstrain of the synthesized samples was calculated using Williamson–Hall analysis [44] and the values are inserted in table 2. Like orthorhombic deformation, the microstrain was also found to increase gradually with milling time [45] and for 12 h ball milling sample the microstrain is significantly higher.

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6 Supplemental table I shows the ideal composition and elemental composition of Gd0.7Sr0.3MnO3 for bulk materials, nanoparticles prepared by ultrasonication, ball milling techniques. Figure I (S1) shows block diagram of a system with transfer function $h(n)$. Supplemental table II shows the maximum magnetization $M_0$ of Gd0.7Sr0.3MnO3 at 50 kOe for bulk materials, nanoparticles prepared by ultrasonication and ball milling techniques.
standard sample. But a completely crystalline sample has some background intensity, which arises from imperfections of the sample, the x-ray optics of the instrument, sample fluorescence and scattering. Therefore, X Pert HighScore Plus, the background is calibrated with the granularity of 22 and a bending factor of 5 hence is applied to the correction for all the samples. The following equation was involved for amorphousity calculation

\[
\text{Amorphosity\%} = 100 - [100 \times \frac{I_{\text{net}}}{I_{\text{tot}} - I_{\text{const.bg}}}] 
\]

where \(I_{\text{net}}\): crystal intensity; \(I_{\text{const.bg}}\): background intensity; \(I_{\text{tot}}\): total intensity. Then the wt% of crystalline and amorphous phases have been normalized (100%) to obtain the wt% of all other phases inside the samples. The wt% of crystalline and amorphous phases are inserted in Table 2. The amorphization % nominally increase for nanoparticles prepared by ultrasonication and 4 h ball milling compared to that of bulk materials. However, for a milling time of 8 h and 12 h, the amorphous phase formation is nearly three times higher compared to that of bulk materials. For 8 h and 12 h milling time, the amorphous phase is around 33.2 wt% and 35.9 wt%, respectively as shown in Table 2.

Rietveld refinement has also been performed to estimate the amount of other oxides presence in these manganites. The wt% of other oxides obtained after refinement was inserted in Table 2. In the bulk materials apart from orthorhombic Gd_{0.7}Sr_{0.3}MnO_{3} (84.5 wt%) manganites, the refined data shows the presence of SrO_{2} (3 wt%). For 4 h ball milled nanoparticles, along with orthorhombic Gd_{0.7}Sr_{0.3}MnO_{3} (78.1 wt%) manganites, a fair amount of Mn_{2}O_{3} (5.2 wt%) is formed. For a longer milling time of 8 h and 12 h, the amount of Mn_{2}O_{3} is reduced significantly, however, the amorphization, orthorhombic deformation and microstrain increase noticeably as mentioned earlier. In the ultrasonically prepared nanoparticles, the orthorhombic Gd_{0.7}Sr_{0.3}MnO_{3} phase is 83.2 wt% along with a small amount of other oxides. In Figures 2(a)–(e), the vertical lines demonstrate the Bragg positions of these oxide materials along with orthorhombic Gd_{0.7}Sr_{0.3}MnO_{3} manganites.

Figure 3(a) demonstrates the surface morphology of the pellets of Gd_{0.7}Sr_{0.3}MnO_{3} bulk perovskite manganites. The surface of the pellets are pretty homogeneous and the average grain size is around 1–1.5 μm. Figure 3(b) shows FESEM image of Gd_{0.7}Sr_{0.3}MnO_{3} particles prepared by ultrasonication, images (b)–(e) show particle size for 4 h, 8 h and 12 h ball milling, respectively. The distribution of the ultrasonically and ball milled nanoparticles deduced from micrographs are also shown in images (b)–(e). The size of the ultrasonically prepared nanoparticles is estimated from the distribution histogram of figure 3(b) is 50–100 nm. The average size of the nanoparticles prepared by 4 h ball milling is also ranging from 50–100 nm. For a further increase of the milling time, the overall distribution of the particle size histogram did not change significantly, however, agglomeration of powder materials increase with milling time [47]. In the present investigation, the calculated size of the ultrasonically prepared particles from the FWHM of (200) peak of XRD pattern using Scherrer’s formula [48] is ~27 nm which is much smaller than the value observed from FESEM image. The large particle size determined by electron microscopy images compared to that calculated by Scherrer equation has also been reported in previous investigations [49, 50] and this was due to the agglomeration of the particles. For ball milled nanoparticles, broadening of the (200) peak is also associated with microstrain as well as amorphization of the material. Therefore, we have not calculated the crystallite size of the ball milled nanoparticles using Scherrer equation.

Notably, the EDX analysis presented also in the supplemental table 1 reveals the presence of Gd, Sr, Mn, and O elements in bulk materials as well as in ultrasonically prepared nanoparticles. However, the compositional analysis of the ball milled nanoparticles also confirms the presence of Zr along with Gd, Sr, Mn, and O. The Zr was contaminated during ball milling and the amount of Zr was increased with increasing milling time.

Figure 4 demonstrates the O 1 s XPS spectra of (a) bulk polycrystalline Gd_{0.7}Sr_{0.3}MnO_{3} manganites, (b) ultrasonically prepared nanoparticles and (c)–(e) ball milled nanoparticles for 4 h, 8 h and 12 h, respectively. The O 1 s XPS spectra of bulk polycrystalline Gd_{0.7}Sr_{0.3}MnO_{3} manganites show a slightly asymmetric peak very close to 529.5 eV along with an additional peak. The asymmetric curves of the bulk sample can be Gaussian fitted by two symmetrical peaks at 529.3 eV and 530.8 eV, respectively (Figure 4(a)). The lower binding energy peak at 529.3 eV corresponds to O 1 s core spectrum, while higher binding energy peak is attributed to the oxygen vacancies i.e. to the oxygen related defects [31, 52] in the sample. Interestingly, in the case of Gd_{0.7}Sr_{0.3}MnO_{3} nanoparticles prepared by ultrasonication we have observed a symmetrically single XPS peak (Figure 4(b)) of O 1 s [53, 54]. This indicates the absence of oxygen vacancy in ultrasonically prepared Gd_{0.7}Sr_{0.3}MnO_{3} nanoparticles. Similar to the ultrasonically prepared nanoparticles, the ball milled nanoparticles do not show any peak corresponding to oxygen vacancy. It is expected that the presence and absence of oxygen vacancies [31] in Gd_{0.7}Sr_{0.3}MnO_{3} bulk materials and their nanoparticles, respectively will affect the mixed Mn^{3+}/Mn^{4+} valence state which ultimately influences their magnetization [30].

See footnote 6.
3.2. Magnetic properties

To investigate the phase transition temperatures of bulk materials and corresponding synthesized nanoparticles, the temperature dependent magnetization measurements were carried out. Figures 5(a)–(c) demonstrate the temperature dependent magnetization (M–T) curves of Gd0.7Sr0.3MnO3 bulk materials, and nanoparticles prepared by ultrasonication and by ball milling of bulk powder materials for 4 h, respectively in ZFC and FC processes. The temperature dependent ZFC and FC curves of 8 h and 12 h ball milled nanoparticles are shown in figure 5(d). To perform the experiment in the ZFC process, the sample was initially cooled from 300 K to 5 K and data were collected while heating in the presence of the applied field. On the other hand, in the FC mode, data were collected while cooling in the presence of a 500 Oe magnetic field. In the case of bulk (figure 5(a)) as well as nanoparticles prepared by ultrasonication technique (figure 5(b)), a clear splitting between ZFC and FC magnetization curves were observed below 42–47 K under the application of a magnetic field of 500 Oe. The splitting of ZFC and FC curves for 4 h ball milled nanoparticles started at higher temperature i.e. 70–75 K. The splitting of the curves suggests that Gd0.7Sr0.3MnO3 bulk materials and their corresponding nanoparticles are in a
spin-glass-like state \[11, 33, 55\] at lower temperatures. Moreover, the temperature dependent magnetization curves exhibit a paramagnetic to spin-glass like splitting transition for both bulk powder materials and ultrasonically prepared nanoparticles at temperatures \(T_g = 35–40\) K. The value of the transition temperature is consistent with value reported elsewhere \[32\] for the same manganite system. However, for 4 h balled milled nanoparticles, the phase transition is observed at a relatively higher temperature (38–48 K) as seen in figure 5(c). Moreover, on either side of this transition temperature, a different trend of the temperature variation of magnetization than that of bulk and ultrasonically prepared nanoparticles is observed. Notably, in the case of nanoparticles prepared by 8 h and 12 h ball milling, both ZFC and FC curves coincide with each other throughout the temperature range. Beside this, nanoparticles prepared by ball milling for milling time 8 h and 12 h does not show any phase transition, rather a small upturn to 0.6 emu g\(^{-1}\) is observed at low temperature. The steep increase of magnetization at low temperature may correspond to the paramagnetic contribution of the \(\text{Gd}^{3+}\) moments \[56\]. In this way, the magnetic behavior of the nanoparticles synthesized by ball milling technique is different from those of bulk materials and ultrasonically prepared nanoparticles.

To further explore the difference between the magnetic properties of bulk materials and nanoparticles synthesized by two different techniques, we have carried out field dependent magnetization measurements. The magnetization versus magnetic field (M–H) hysteresis loops of \(\text{Gd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) bulk materials and nanoparticles prepared by ultrasonication and ball milling techniques were carried out at 300 K and 20 K, figures 6(a) and (b), respectively. At 300 K, the unsaturated linear curves without any detectable hysteresis as shown in figure 6(a) indicate the paramagnetic nature of \(\text{Gd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) bulk powder materials and their corresponding ultrasonically prepared and ball milled (8 h and 12 h) nanoparticles. However, for 4 h ball milled nanoparticles, a tiny hysteresis loop is observed at 300 K which is clearly different from that of other materials under investigation. The maximum magnetizations \(M_s\) of \(\text{Gd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) at 50 kOe for bulk materials and nanoparticles prepared by ultrasonication and ball milling are inserted in supplemental table 2.\(^{8}\) Notably, at 300 K, the magnetization of 4 h ball milled nanoparticles is anomalously higher compared to that of other materials and it is anticipated that the presence of 5.2 wt\% Mn\(_2\)O\(_3\) may influence the magnetic behavior of this sample. The Mn\(_2\)O\(_3\) is an antiferromagnetic material with a Néel temperature of 80–100 K \[57\]. We think that at 300 K, the 4 h ball milling sample is dominated by superparamagnetic behavior, presumably due to Mn\(_2\)O\(_3\). Apart from this anomalous behavior, the magnetization is higher in bulk materials compared to that of nanoparticles prepared by ultrasonication as well as ball milling for milling time 8 h and 12 h.

\(^{8}\) See footnote 6.

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**Figure 5.** Temperature dependence of magnetization (M–T curves) of \(\text{Gd}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\) (a) bulk materials, (b) ultrasonically prepared nanoparticles, (c) 4 h ball milled nanoparticles and (d) 8 h and 12 h ball milled nanoparticles in ZFC and FC processes.
The higher value of magnetization in bulk materials may be associated with its good crystallinity. In ultrasonically prepared nanoparticles, the amorphization is minimum compared to ball milled nanoparticles, and a reduction in magnetization is observed. For 8 h and 12 h ball milled nanoparticles, the amorphization is significant. Therefore, we think that the drastic decrease in magnetization in ball milled (8 h and 12 h) nanoparticles is associated with the amorphization of the ball milled nanoparticles. It is worth mentioning that similar class of nanoparticles of La$_{0.7}$Ca$_{0.3}$MnO$_3$ \cite{14} and La$_{0.8}$Sr$_{0.2}$MnO$_{3-\delta}$ \cite{18} manganites were prepared by using ball milling from bulk polycrystalline samples. In these investigations, the particle size was found to decrease with milling time and for a longer milling time (>8 h), the crystalline particle size was reduced. In addition to these, the ferromagnetic to paramagnetic transition temperatures, i.e., $T_c$ values of La$_{0.7}$Ca$_{0.3}$MnO$_3$ nanoparticles prepared by ball milling were found to decrease compared to those of unmilled bulk polycrystalline powder materials. Moreover, magnetization of the nanoparticles synthesized by ball milling was decreased dramatically compared to the bulk polycrystalline samples. A previous investigation also reported the magnetic properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCM) thin films with structural disorder \cite{58}. In these reports, it was observed clearly that amorphous LCM thin film demonstrated a paramagnetic behavior whereas the crystalline film exhibited a cluster-spin-glass state \cite{58}. It is also reported that the properties of nanocrystalline manganites thin films are comparable with that of nanopowders \cite{21}.

The magnetization measurement at 20 K, figure 6(b), demonstrates hysteresis with significant coercivities in bulk materials and their corresponding nanoparticles prepared by ultrasonication technique. At 20 K, the 4 h ball milled nanoparticles also exhibits a hysteresis loop with a large coercivity. In this investigation, at 20 K, the coercive fields ($H_c$) are 1500 Oe, 910 Oe and 540 Oe for ultrasonically prepared nanoparticles, and bulk materials and 4 h ball milled nanoparticles, respectively (inset of figure 6(b)). In fact, the coercive fields are temperature dependent \cite{59} and these increase with decreasing temperatures \cite{60}. Previous investigation also demonstrated that the coercive field increases with decreasing particle size \cite{61}. In our investigation, at 20 K, the coercive field is higher for ultrasonically prepared nanoparticles compared to that of bulk materials as was also observed in \cite{20} for similar La$_{0.7}$Ca$_{0.3}$MnO$_3$ manganite system. In the case of nanoparticles prepared by ball milling technique with milling time 8 h and 12 h, the M–H curve is just a straight line with zero coercivity both at 300 K and 20 K as shown in figures 6(a) and (b), respectively.

In rare-earth based perovskite manganites, the presence of Mn$^{3+}$ ions, due to the doping, enables itinerant eg electron of a Mn$^{3+}$ to hop to the neighbouring Mn$^{4+}$ through oxygen ion \cite{30} and thus mediate magnetism and conductivity. The presence of oxygen vacancies in Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ bulk manganites is expected to enhance the conversion of a proportional number Mn$^{3+}$ to Mn$^{4+}$ \cite{31} and hence we observe higher value of the magnetization in bulk materials. Notably, the ultrasonically prepared nanoparticles are still good in terms of magnetization despite having apparently no oxygen vacancies. It may be expected from XPS measurement, figure 4, that from the surface of the nanoparticles, vacancies have been removed, while in the core of the nanoparticles it may still be present. More specifically, at 500 eV, the electron escape depth is about 5 nm and hence XPS indicates vacancies that have been removed from the particles’ surface while the core volume may still have the vacancies of the bulk.

4. Conclusions

By using ultrasonication technique, rare-earth based Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ nanoparticles were produced directly from their bulk powder materials and the chemistry of the particles were likely unaltered apart from the absence of detectable surface oxygen vacancies. Hence, bulk and nanoparticle materials were more directly comparable in...
Gd$_{0.7}$Sr$_{0.3}$MnO$_3$ nanoparticles demonstrate the potential of this synthesis route for the fabrication of these complex size, crystallinity, amount of major phase formation, unaltered phase transition etc. of ultrasonically prepared as well as their bulk materials which may be associated with the amorphization and contamination of the ball milled 8 h and 12 h ball milling is found to decrease drastically compared to the ultrasonically prepared nanoparticles as anomalously different as compared to that of other materials. The magnetization of the nanoparticles prepared by ball milling facility.

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