Multiple magnetic transitions and magnetocaloric effect in hydrothermally synthesized single crystalline La_{0.5}Sr_{0.5}MnO_{3} nanowires

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ABSTRACT
We have successfully prepared La_{0.5}Sr_{0.5}MnO_{3} nanowires using a novel hydrothermal synthesis process and studied their magnetic and magnetocaloric properties. The system exhibits an inverse magnetocaloric effect (IMCE) around 175 K indicating presence of significant AFM correlation. The MCE study reveals a clear paramagnetic (PM) to ferromagnetic (FM) transition near room temperature (T ~ 325K) which is followed by onset of AFM at lower temperatures. The development of the FM-like magnetic state at low temperature is attributed to the enhanced double exchange (DE) driven ferromagnetism in AFM state as predicted by recent theoretical studies.

INTRODUCTION
The physics of mixed valence perovskite manganites with a general formula R_{1-x}B_{x}MnO_{3} (R – rare earth, B- bivalent ion) has been a topical area of research over the last few decades [1]. These systems possess very rich physical properties as a result of the interplay between many complex interactions. In addition to this, manganites exhibit many intriguing phenomena such as colossal magnetoresistance (CMR), giant magnetocaloric effect (MCE) etc, which have direct relevance in different practical applications [1-2].

A current trend of research in this area is to understand the modification in the properties of these systems when they are synthesized in nanostructured forms [3-14]. In this regard, the systems were mostly studied in the forms of nanoparticles and thin films (~ nm thickness) [3-14]. However, recently there have been reports regarding successful synthesis of manganite nanowires and the investigation of their properties in comparison to their bulk counterpart [11, 15-18].

In addition to the different physical and electronic properties, the magnetocaloric properties of manganites attract considerable research interest [2]. Magnetic refrigeration based on the MCE of a magnetic material is considered as a promising alternative to conventional gas compression refrigeration technology and it is believed that manganites have most of the essential characteristics desirable in potential magnetic refrigerants. Besides the application perspective, the study of MCE in manganites is interesting from a fundamental point of view as it can provide valuable information to understand the complex magnetic properties of these systems [3, 19]. Moreover, such study is often helpful to probe different magnetic phase transitions and competing magnetic phases, which may not be easily determined by other

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conventional experiments such as dc magnetization, transport etc. [3]. Although there are a few reports highlighting investigation of MCE in nanoparticles and thin films of manganites [19-21], there is hardly any such study on the systems in the form of nanowires.

The main objective of the present work is to carry out an experimental investigation of magnetocaloric properties of manganite nanowires. In this regard, we have studied MCE of hydrothermally synthesized La0.5Sr0.5MnO3 (LSMO) nanowires. One of our important observations is that the LSMO nanowires show a signature of antiferromagnetism by exhibiting an inverse magnetocaloric effect (IMCE), which is very rare in case of nanostructured manganites.

**SAMPLE PREPARATION AND CHARACTERIZATION**

The nanowires of La0.5Sr0.5MnO3 were prepared by novel hydrothermal method from starting materials La(NO3)3, MnCl2, KMnO4 and Sr(NO3)2 [15-16]. We used KOH as mineralizer in the synthesis process. In the first step of the process, KOH was added in the water solution of the starting materials in suitable molar ratio. Then the mixture was intensively stirred and put inside a Teflon vessel. Subsequently the hydrothermal treatment was carried out by having the vessel inside a stainless steel autoclave. The crystallization process was continued at around 500K for 50 hours and then the autoclave was allowed to cool down and depressurize. Finally the product was thoroughly washed with deionized water, followed by drying at 390 K to obtain nanowires. The formation of the nanowires was confirmed by x-ray diffraction study (XRD) (Fig. 1A). Scanning Electron Microscopy (SEM) enabled us to estimate the mean diameters of the wires as well as their lengths. The nanowires of 50 -300 nm diameter were prepared in this process with length varying from 1-10 micron. We further confirmed the preparation of highly crystalline nanowires through High Resolution Transmission Electron Microscopy (HRTEM) and electron diffraction studies. A typical SEM image along with a HRTEM image of the prepared nanowires is shown in Fig. 1B.

![X-ray diffraction pattern of the prepared La0.5Sr0.5MnO3 nanowires](A)

![A typical SEM image of the nanowires](B)

Figure 1: (A) X-ray diffraction pattern of the prepared La0.5Sr0.5MnO3 nanowires. (B) A typical SEM image of the nanowires. The inset shows a HRTEM image of a selected position of a nanowire.
RESULTS AND DISCUSSIONS

Isothermal magnetization \([M(H)]\) was measured using a commercial Physical Property Measurement System (Quantum Design) over the temperature range 10-340 K in magnetic fields up to 5T. \(M(H)\) curves taken at some selected temperatures are shown in Fig. 2. MCE in a material can be parameterized by the change in magnetic entropy \((\Delta S_M)\) associated with a change in applied magnetic field, which can be calculated from a set of isothermal \(M(H)\) curves using the following Maxwell’s relation [2]:

\[
\left\langle \frac{\partial S(T, \mu_0 H)}{\partial \mu_0 H} \right\rangle_T = \left\langle \frac{\partial M(T, \mu_0 H)}{\partial T} \right\rangle_{\mu_0 H} \tag{1}
\]

For a magnetic material, PM to FM transition is associated with a decrease of magnetic entropy due to increase in applied field. However in an AFM transition, the calculated entropy change \((\Delta S_M)\) is positive for applied fields lower than that for quenching of the AFM state. The consistent increase in magnetic entropy with the application of magnetic field is known as an inverse magnetocaloric effect (IMCE). The materials exhibiting IMCE would be very useful as refrigeration capacity can be improved by using these materials along with conventional ferromagnetic refrigerants [2, 21, 22].

Figure 2: Representative M(H) curves at some selected temperatures. All curves are not included for sake of clarity.

We have calculated the temperature dependence of \(\Delta S_M\) for different applied magnetic fields from a family of isothermal \(M(H)\) curves using Eq. (1). Fig. 3 shows \(-\Delta S_M(T)\) for the magnetic field changes of 1T, 3T, and 5T. There exists signatures of three distinct magnetic transitions in \(-\Delta S_M(T)\): two maxima at ~290 K and 45 K; a minimum at ~175 K. The maximum at ~290 K can be attributed to the occurrence of a PM-FM transition in the sample. For bulk La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\), the PM-FM transition occurs above room temperature. Perhaps the most interesting feature of \(-\Delta S_M(T)\) for the present nanowires is the occurrence of the clear minimum at ~175 K associated with IMCE in the system, which is consistent with an AFM transition that occurs in bulk La\(_{0.5}\)Sr\(_{0.5}\)MnO\(_3\) around that temperature[22, 23]. Hence in analogy of bulk sample, it can be inferred that the IMCE observed in the nanowires also arises due to the AFM transition.
Figure 3: $-\Delta S_{M}(T)$ curves for applied magnetic field of 1, 3 and 5T.

There are many reports in literature highlighting the complete suppression of AFM transition in cases of nanocrystalline and nanowire form of manganites especially when doping level is near 50% [5,8,9-11]. In this context, the development of AFM state in present nanowires is very interesting. Generally for half doped manganites, charge ordered (CO) state is developed at low temperature originating a C-E type AFM state [1]. The CO transition is martensitic-like transition (MT) and it is difficult for nanostructured materials to accommodate strain associated with MT [9, 25]. As a result the formation of CO state is hardly possible in such materials leading to the suppression of AFM state [5,8,9-11]. However in case of La$_{0.5}$Sr$_{0.5}$MnO$_3$, AFM state is A-type and it is not due to CO [1, 23, 24]. Probably as the AFM state for this composition is not related with CO, it can be developed even in nanostructured form of the material. Recent report regarding IMCE due to AFM transition in case of nanocrystalline La$_{0.45}$Sr$_{0.55}$MnO$_3$ is also consistent with present result [22].

We have also observed a maximum in $-\Delta S_{M}(T)$ at a low temperature of $\sim$45 K, which is an indication of FM -like magnetic transition. According to the phase diagram of La$_{1-x}$Sr$_x$MnO$_3$ with $x=0.5$, there should not be any distinct magnetic transition around that temperature range [1]. Thus a question may arise regarding the origin of the $-\Delta S_{M}(T)$ peak at $\sim$45 K in the case of the nanowires. For other manganite systems, the rare-earth atoms order at low temperature giving rise to a magnetic transition [9]. However, for the present sample containing non-magnetic La as a rare-earth ion, such a possibility can be ruled out. For nanostructured materials, the surface effect plays a vital role in determining their magnetic properties. Theoretical studies predict that the unscreened Coulomb interactions cause an enhancement of electron density on the surface leading to an increase of double exchange interaction [10, 12]. Thus electronic reconstruction of surface favours enhancement of ferromagnetism in nanostructured manganites [10, 12]. It can be argued that the onset of ferromagnetism reflected by a clear maximum in $-\Delta S_{M}(T)$ at low temperature for the present nanowires arise as a result of enhanced ferromagnetism in the sample as predicted by theoretical studies [10,12]. Enhanced ferromagnetism has been experimentally observed in nanoparticles and wires of manganites before [13, 17]. Recently a similar phenomenon has been demonstrated for nanocrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$ where IMCE was also observed [21].
CONCLUSIONS

Nanowires of La$_{0.5}$Sr$_{0.5}$MnO$_3$ were successfully synthesized by hydrothermal method and their magnetocaloric properties were studied. The system exhibits IMCE at $\sim 175$ K due to the stabilization of AFM phase. A positive peak is observed at $\sim 290$ K in $-\Delta S_M(T)$ due to FM transition. DE driven ferromagnetism is enhanced at low temperature according to theoretical predictions giving rise to another positive maxima in $-\Delta S_M(T)$.

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REFERENCES


