Magnetocaloric properties of nanocrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$

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Abstract

Some recent experimental studies show the invisibility of antiferromagnetic transition in the cases of manganites when their particle size is reduced to nanometer scale. In complete contrast to these cases, we have observed the signature of antiferromagnetic transition in the magnetocaloric properties of nanocrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$ of average particle size 70 and 60 nm similar to its polycrystalline bulk form. The system exhibit inverse magnetocaloric effect in its polycrystalline and nanocrystalline form. An extra ferromagnetic phase is stabilized at low temperature for the sample with particle size $\sim$ 60 nm.

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The physics of Perovskite Manganites has been a intriguing subject of intense research from both fundamental and application points of view [1]. A recent trend of research in the field of manganites is to study the effect of the reduction of particle size on different properties of the materials [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. It has already been reported that the particle size can have significant influence on the different phenomena exhibited by manganites [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20]. As a result, the transport, magnetic, magnetotransport and magnetocaloric properties of those materials are observed to be markedly modified when the particle size is reduced to the nanometer scale. The main objective of the present study is to investigate the effect of the lowering of particle size on the magnetocaloric properties of La$_{0.125}$Ca$_{0.875}$MnO$_3$. In fact, the study of magnetocaloric properties of materials stimulates considerable research interest owing to its possible application in the magnetic refrigeration [21, 22, 23, 24, 25, 26, 27, 28, 29].

It has been reported that polycrystalline bulk La$_{0.125}$Ca$_{0.875}$MnO$_3$ shows paramagnetic to antiferromagnetic transition at $\sim 125$ K with the lowering of temperature [1]. There is influence of the presence of inhomogeneous canted antiferromagnetic state on the antiferromagnetic transition for this compound [1]. We have observed inverse magnetocaloric effect (IMCE) i.e, minimum in $-\Delta S(T)$ in the vicinity of antiferromagnetic (AFM) transition temperature for the polycrystalline bulk form of the sample. Such a minimum in $-\Delta S(T)$ is visible for its nanocrystalline forms around the same temperature as bulk also, which implies the occurring of antiferromagnetic transition for the nanoparticles of this manganite system. In addition to IMCE, a maximum in $-\Delta S(T)$ arises at low temperate in the cases of nanocrystalline sample with the lowest particle size indicating stabilization of ferromagnetic state. The observation of clear signature of AFM transition for La$_{0.125}$Ca$_{0.875}$MnO$_3$ nanoparticles directly contradicts the previous experimental results of invisibility of AFM transition for many manganites due to the reduction of particle size [3, 6, 7, 8, 9, 10, 13, 15].

The polycrystalline and nanocrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$ were prepared by solgel method. The details of the solgel method has been described in our previous article [3]. At the end of the solgel process, the decomposed gel was annealed at $1400^\circ$C for 36 hours to prepare the polycrystalline sample. However, for preparing the nanoparticles of two different average particle size, the decomposed gel was subjected to heat treatment at 1200 and $1000^\circ$C for 6 hours. The x-ray powder diffraction study has confirmed the formation of the
samples with single crystallographic phase. The particle size of the nanocrystalline samples was determined by Scanning Electron Microscopy (SEM) study. The average particle size of the nanocrystalline sample prepared at 1200°C is ∼70 nm. On the other hand, the average particle size of the sample synthesized at 1000°C is ∼60 nm. The two nanocrystalline samples are designated as S70 (sample with particle size ∼70 nm) and S60 (sample with particle size ∼60 nm) respectively. The typical SEM micrographs of the two samples have been given in Fig. 1.

A commercial SQUID magnetometer was utilized for magnetization measurements. The isothermal magnetic field dependence of magnetization [M(H)] at different temperatures has been studied for the samples (Fig. 2). From the isothermal M(H) curves, the change of the magnetic entropy (-∆S) was estimated for various magnetic fields by using the Maxwell’s relation [24],

\[
\left( \frac{\partial S}{\partial \mu_0 H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_{\mu_0 H}
\]

The temperature dependence of -∆S for 7 T has been shown in Fig. 3. A minimum in -∆S(T) (inverse magnetocaloric effect) has been observed at ∼125 K for the polycrystalline as well as the nanocrystalline samples. The materials exhibiting IMCE would be very useful for magnetic refrigeration as the refrigerant capacity can be enhanced by utilizing those materials in composite with the conventional magnetic refrigerants [29]. However, the manifestation of IMCE in the cases of manganites is rare. For the polycrystalline La0.125Ca0.875MnO3, antiferromagnetic transition occurs at ∼125 K [1]. In the cases of antiferromagnetic systems, when the applied magnetic field is below the field required for the quenching of antiferromagnetism, the IMCE can be observed [30]. The IMCE for the present polycrystalline sample originates due to the antiferromagnetic transition. Similarly, the minimum in -∆S(T) around the same temperature as the polycrystalline sample for S70 and S60 can be considered as the signature of the antiferromagnetic transition. There are number of studies on different nanocrystalline systems, which reveal that the antiferromagnetic transition in bulk system becomes invisible due to the reduction of particle size. The present result for the nanocrystalline La0.125Ca0.875MnO3, contradicts those existing results. The stabilization of antiferromagnetic state in the previous systems is mostly of C-E type and arises as because of the occurrence of charge order transition (COT). In their nanocrystalline form, COT does not occur resulting in the hin-
The phase diagram of La$_{1-x}$Ca$_x$MnO$_3$ reveals that La$_{0.125}$Ca$_{0.875}$MnO$_3$ situates at the phase boundary and charge ordering correlation is hardly present in this compound [1]. The antiferromagnetic state originated in this compound is mixture of C-type and G-type. From the present result, it seems that because of different type of antiferromagnetic ordering for La$_{0.125}$Ca$_{0.875}$MnO$_3$ in comparison to the charge ordered antiferromagnetic state for previous cases, the antiferromagnetic transition can be visible in the nanocrystalline form of this material. An additional feature of $-\Delta S(T)$ for S60 is a clear maximum in low temperature. Such a maximum is an indication of the onset of ferromagnetism for that nanocrystalline sample. Very recent theoretical study predicts that the ferromagnetic correlation can be originated due to the surface effect in the cases of fine particles of manganites [10]. The signature of ferromagnetism at low temperature in the $-\Delta S(T)$ observed for S60 can be attributed to the surface effect in accordance to the theoretical prediction [10]. For the nanocrystalline samples, the surface effect becomes more dominant as the particle size of the sample reduces. It appears that the surface effect for S70 is not so enough to create ferromagnetic state. However in the case of S60 with lower particle size, surface effect can be more dominant giving rise to ferromagnetism at low temperature. The M-H curves at 45 K and 95 K for the two samples are also different. There is a cross over between M-H curves at 45 K and 95 K in the low magnetic field region for S70 like its bulk form. This cross over between two M-H curves is absent for S60 (Fig. 2).

To summarize, we have observed IMCE for polycrystalline as well as nanocrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$ due to the antiferromagnetic transition. The evidence of antiferromagnetic transition in the cases of nanocrystalline manganites is in direct contradiction of existing experimental results for different manganite systems [3, 6, 7, 8, 9, 10, 13, 15, 16]. Reduction of particle size has also pronounced effect on the magnetocaloric properties of this material as an additional maximum is visible in $-\Delta S(T)$ for the sample with average particle size 60 nm. The observation of IMCE is very rare especially in the cases of rare-earth based manganites.
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FIG. 1: Scanning electron micrograph for nanocrystalline La$_{0.125}$Ca$_{0.875}$MnO$_3$ of average particle size (a) 70 nm and (b) 60 nm. The samples of average particle size $\sim$ 70 nm and $\sim$ 60 nm are designated as S70 and S60 respectively.

FIG. 2: M versus H curves at some temperatures for (a) polycrystalline bulk (b) S70 and (c) S60. M(H) curves at other temperatures are not shown because of sake of clarity.

FIG. 3: The temperature dependence of $-\Delta S$ for 7 T in the cases of (a) polycrystalline bulk, (b) S70 and (c) S60.
FIG. 1:
FIG. 2:
FIG. 3: