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NEAR ROOM-TEMPERATURE TEMPERATURE MAGNETOCALORIC EFFECT IN $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ MANGANITES

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ABSTRACT. Near room-temperature magnetic and magnetocaloric properties of the compounds $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ (x=0, 0.05) were investigated. The parent compound $Pr_{0.63}Sr_{0.37}MnO_3$ has a large magnetocaloric effect around its Curie temperatures of about 300 K. Partially replacing of Pr^{3+} ions with Ho^{3+} ions in $Pr_{0.63}Sr_{0.37}MnO_3$ gives rise to disorder which leads to the decrease of the Curie temperature without a significant reduction of the magnetocaloric effect. The samples were prepared by solid state reaction and were found to be single phase by x-ray diffraction. The magnetic measurements reveal paramagnetic to ferromagnetic second order phase transitions. For the sample with x = 0, the magnetic entropy change $|\Delta S_M|$ was in the range from 1.91 J/kg⋅K (RCP = 42 J/kg) forμ_0 ΔH = 1 T to 4.86 J/kg⋅K (*RCP* = 184 J/kg) for μ_0 ΔH = 4 T. For the sample with x = 0.05, the magnetic entropy change $|\Delta S_M|$ was in the range from 1.61 J/kg⋅K (*RCP* = 57.9 J/kg) forμ_0 ΔH = 1 T to 4.38 J/kg⋅K (*RCP* = 236 J/kg) for μ_0 ΔH = 4 T and T_c = 216 K. These values recommend these materials to be potential candidates to be used in near room-temperature refrigeration applications.

Keywords: *Perovskite manganites, phase transition, magnetocaloric effect.*

INTRODUCTION

Magnetocaloric effect (MCE) is a magneto-thermodynamic phenomenon which consists in the (irreversible) change of the temperature of a material when a magnetic field is applied. When cooling result in a cycle which consist in magnetization and demagnetization of the magnetocaloric material, this effect can be used as an alternative of the conventional vapor compression domestic refrigerators [1]. Magnetic

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cooling is seen as an alternative for the conventional vapor compressing domestic refrigerators which usually work 20 -30 ^{0}C below room temperature. Gadolinium was found to show the largest magnetocaloric effect in the range from 270 to 310 K with a relative cooling power (RCP) of the order of 240 J/kg but the cost of this material is prohibitive of about 3000 euro/kg [2]. In the last decade a great deal of interest was devoted to find such materials with large MCE and reasonable costs [2]. Large magnetic entropy changes were also found in the perovskite mixed valence manganese oxides or in $Ln_{1-x}A_xMnO_3$ manganites (where Ln is a lanthanide and A is a divalent alkali) [3]. Some of these manganese oxides show large $|\Delta SM (T;\mu_0 H)|$ values comparable to those of the intermetallic compounds (i.e., $|\Delta SM (T;\mu_0 H)| \sim 4–6$ J kg^{-1}K^{-1} when $\mu_0 \Delta H = 5$ T) [4].

Here we propose such a magnetocaloric material, the $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ perovskite manganite where x =0; 0.01. The parent compound is ferromagnetic below Curie temperature which is closed to 300 K and has a large MCE around this T_C. The partially substitution of Ho^{3+}ions (atomic radius 1.75 Å) for Pr^{3+} ions (atomic radius 1.18 Å) generates structural disorder which result in the decrease of Curie temperature to be in the range of the conventional domestic refrigeration.

In this paper we analyze in detail the magnetic and magnetocaloric properties of the $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ perovskite manganites which are promising for application in magnetic cooling.

EXPERIMENTAL

The samples with nominal compositions $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ with x = 0; 0.05 were prepared by standard solid-state reaction from high purity amounts of Pr_6O_{11}, $SrCO_3$, Mn_2O_3 and Ho_2O_3. The powders were mixed and calcinated at 1000^0 C (24 h), then they were pressed in into pellets and sintered at 1300^{0}C (30 h). The samples were checked by x-ray powder diffraction at room temperature by using a Brucker Advance D8 AXS diffractometer with CuKα radiation. A commercial cryogen-free VSM magnetometer (Cryogenic Ltd.) was used for magnetic measurements in the temperature range from 100 to 500 K and in applied magnetic fields from 0 to 4 T.

The magnetocaloric effect was estimated, calculating the magnetic entropy change $\Delta S_M (T,\mu_0 H)$ when the applied magnetic field $\mu_0 H_0$ is turn off to zero. The isothermal $M(\mu_0 H)$ curves were measured at a temperature interval of 5 K around the magnetic transition. In the case of second order magnetic phase transitions, the magnetic entropy change is given by [1]:

$$\Delta S_M(T,\mu_0 H_0) = \frac{1}{\Delta T}\int_0^{\mu_0 H_0}[M(T+\Delta T,\mu_0 H) - M(T,\mu_0 H)]d(\mu_0 H) \quad (1)$$

The relative cooling power (RCP) measures the heat transfer between warm and cold sources and can be calculated with the formula:

$$RCP = \Delta S_M(\max) \times \delta T_{FWHM} \quad (2)$$

$\Delta S_M(\max)$ is the peak value of ΔS_M (T,$\mu_0 H$) and δT_{FWHM} is the full width at half maximum (FWHM) of ΔS_M (T,$\mu_0 H$) vs. T curve for a given applied field. A good magnetocaloric material, needs both a large value of ΔS_M as well as a broad $\Delta S_M(T)$ curve.

RESULTS AND DISCUSSION

The x-ray diffraction patterns indicated that the samples are perovskite and they are single phases as shown in Fig. 1. The samples have orthorhombic *Pbnm* type structure, with the lattice constants a = 5.429 Å; b = 7.667 Å; c = 5.470 Å, for x = 0 and a = 5.432 Å; b = 7.673 Å; c = 5.476 Å, for x = 0.05.

In Figs. 2 and 3 are shown the temperature dependences of magnetization for the two samples taken in 0.05 T. The Curie temperatures are estimated as the point where the derivatives of the $M(T)$ curves dM/dT have a minimum, as can be seen in the inset. For the sample with x = 0 we have T_C = 298 K while for x = 0.05 the T_C = 215 K.

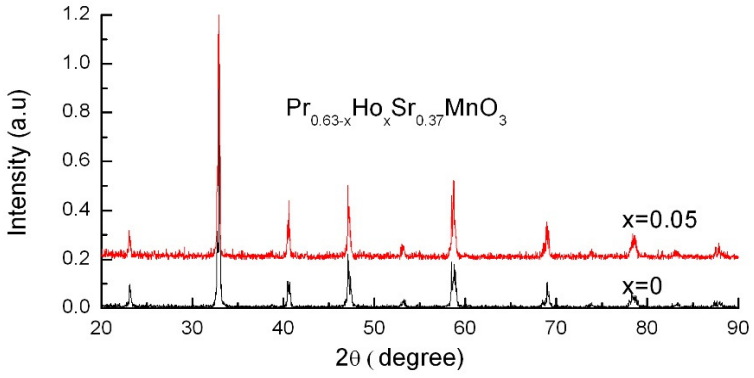

Fig. 1. X-ray diffraction patterns of the $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ samples with x = 0; and x = 0.05.

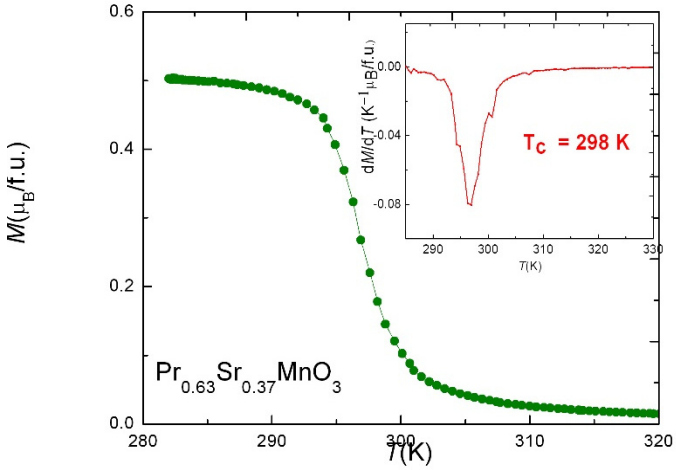

Fig. 2. *M(T)* for $Pr_{0.63}Sr_{0.37}MnO_3$ sample measured in 0.05 T. Inset: d*M*/d*T* vs. *T.*

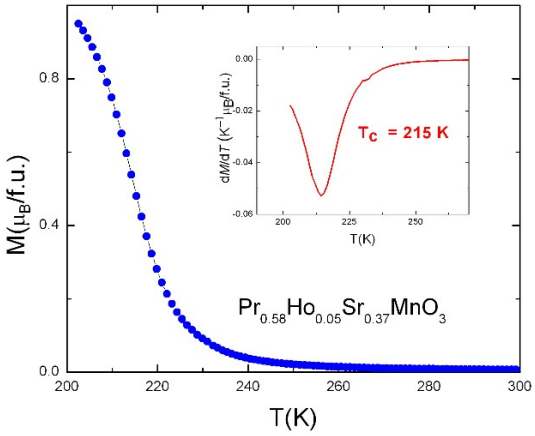

Fig. 3. *M(T)* for $Pr_{0.58}Ho_{0.05}Sr_{0.37}MnO_3$ sample measured in 0.05 T. Inset: d*M*/d*T* vs. *T.*

The magnetic field dependence on magnetization $M(\mu_0 H)$ for the two samples are displayed in Figs. 4 and 5.

As can be seen in Figs. 4 and 5, at low temperatures and in high applied magnetic fields the magnetizations tend to saturate [5], but still keeping a small linear increase. This behavior is the consequence of the presence of Pr^{3+} ions in a distorted crystal field [6].

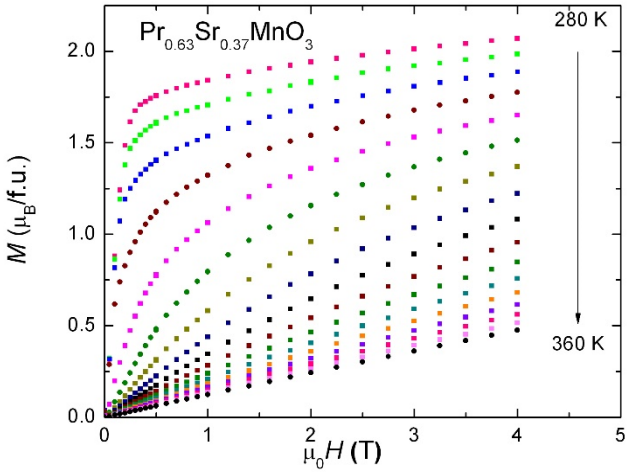

Fig. 4. *M(μ₀H)* for $Pr_{0.63}Sr_{0.37}MnO_3$ sample in the temperature range 280 – 360 K, taken at 5 K interval, from 1 to 4 T

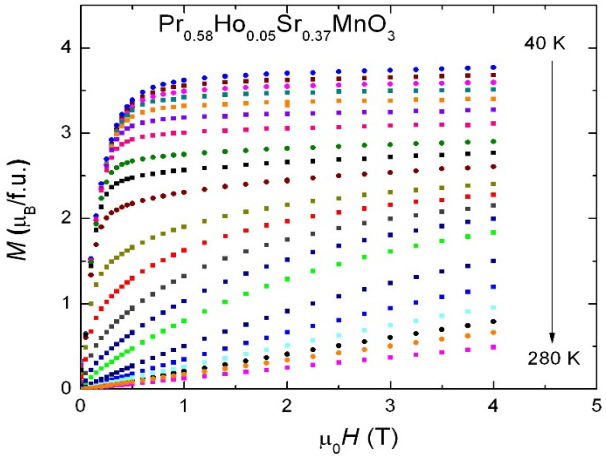

Fig. 5. *M(μ₀H)* for $Pr_{0.58}Ho_{0.05}Sr_{0.37}MnO_3$ sample in the temperature range 40 – 300 K taken at 5 K interval, from 1 to 4 T.

The magnetization dependences on temperature (Figs. 2 and 3) and on applied magnetic field (Figs. 4 and 5), indicate ferromagnetic behavior for the two samples, below the Curie temperatures, with small paramagnetic contributions from Pr^{3+} ions. The magnetocaloric effect can be estimated in terms of magnetic entropy change ΔS_M (T,$\mu_0 H$) and of relative cooling power *RCP*.

The approximation given by formula (1) is valid for a second order magnetic phase transition. The order of a magnetic phase transition can be established analyzing the so-called Arrot plot (M^2 vs $\mu_0 H/M$ around the transition) [7] using the Banerjee criterion [8]. If the slopes of these curves are positive the transition is of second order. If negative slope curves are present the transition is first order.

The Arrot plots for our samples are shown in Figs. 6 and 7.

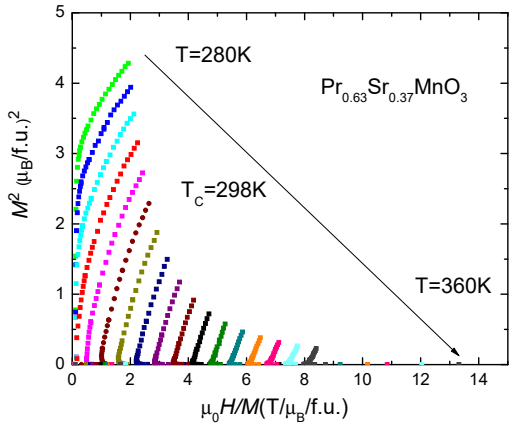

Fig. 6. Arrot plots for $Pr_{0.63}Sr_{0.37}MnO_3$ sample obtained from measured M vs. $\mu_0 H$ isotherms.

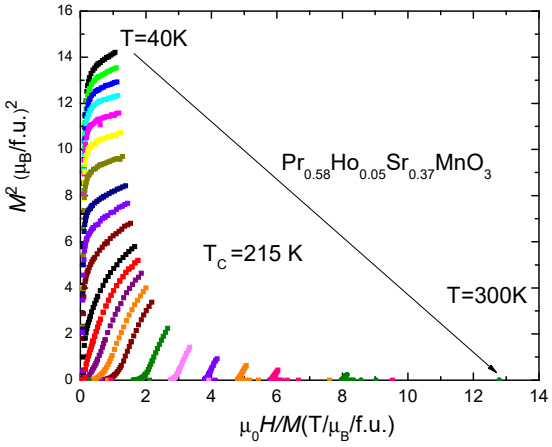

Fig. 7. Arrot plots for $Pr_{0.58}Ho_{0.05}Sr_{0.37}MnO_3$ sample obtained from measured M vs. $\mu_0 H$ isotherms.

As can be seen from these plots all the M^2 vs μ_0H/M curves have positive slopes, indicating the second order character of the phase transition.

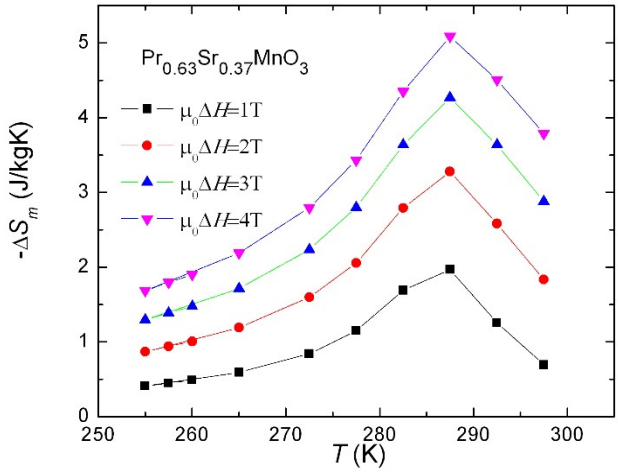

Fig. 8. The magnetic entropy change – ΔSM as a function of temperature for $\mu_0\Delta H$=1,2,3 and 4T, in $Pr_{0.63}Sr_{0.37}MnO_3$.

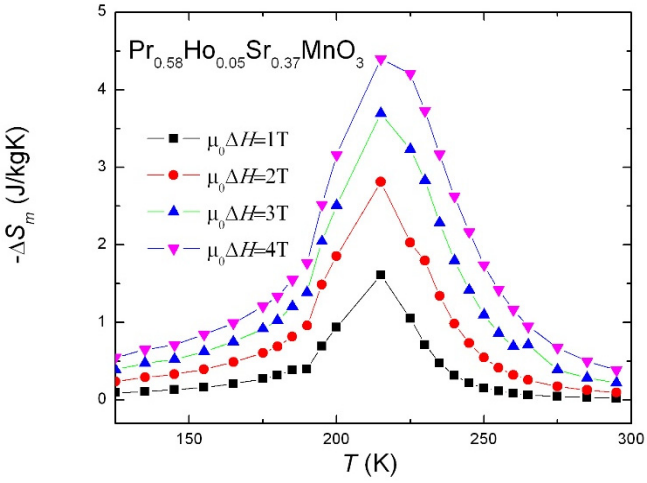

Fig. 9. The magnetic entropy change – ΔSM as a function of temperature for $\mu_0\Delta H$=1,2,3 and 4T, in $Pr_{0.58}Ho_{0.05}Sr_{0.37}MnO_3$.

In these cases, by using the formula (1) we calculated the magnetic entropy change for our samples, and the temperature dependences of $-\Delta S_M(T)$ are plotted for different values of $\mu_0\Delta H$ between 1 and 4 T as shown in Figs. 8 and 9.

The maximum values of magnetic entropy change curves are located in the vicinity of the Curie temperature T_C, for both of ours samples, 298 K for x = 0 and 216 K for x = 0.01. The transition range enlarges in higher applied magnetic fields, and δT_{FWHM} also increases. This behavior results in a large relative cooling power, *RCP,* corresponding to a material with a higher cooling efficiency. The shapes of the $-\Delta S_M$ (T) curves are rather symmetric with respect to the T_C's, which is also important for a magnetic refrigerator. The maximum values of $\Delta S_M(T)$ reach 5.09 J/kg·K (*RCP* = 184 J/kg) for μ_0 ΔH = 4 T for the sample with x = 0 and 4.38 J/kg·K (*RCP* = 236J/kg) for μ_0 ΔH = 4 T for the sample with x = 0.01.

Some quantitative parameters related to magnetocaloric effect in the two samples are given in Tables 1 and 2.

Table 1. T_C, $-\Delta S_M^{max}$, δT_{FWHM} and *RCP* when $\mu_0\Delta H$ = 1, 2, 3 and 4 T for the sample $Pr_{0.63}Sr_{0.37}MnO_3$

$\mu_0\Delta H$ (T)	T_C (K)	$-\Delta S_M^{max}$ (J.kg^{-1}·K^{-1})	δT_{FWHM} (K)	*RCP* (J·kg^{-1})
1	288	1.96	22	42.0
2	289	3.27	24	79.2
3	289	4.26	34	143.5
4	289	5.09	38	184.7

As can be seen from the Table 1 and 2, both the samples show large maximum value of the magnetic entropy change $-\Delta S_M^{max}$. When Ho^{3+} ions substitute for Pr^{3+} the $-\Delta S_M^{max}$.do not depreciate to much (from 5.09 to 4.40 J.kg^{-1}·K^{-1} for $\mu_0\Delta H$ = 4T); *RCP* increases (from 184.7 to 236.5 J·kg^{-1} for $\mu_0\Delta H$ = 4T) and T_C was strongly decreased from 298 to 215 K.

Such a behavior is expected in a compound that presents a large lattice distortion and consequently a strong spin disorder. Since we have a high ionic size mismatch between Pr^{3+} and Ho^{3+} the local disorder created will result in a drastically reduction of Curie temperature and in broadening of the magnetic phase transition. But the strong spin-lattice coupling in $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ compounds may keep large values for the magnetic entropy change, for a large MCE [9].

Table 2. T_C, $-\Delta S_M^{max}$, δT_{FWHM} and *RCP* when $\mu_0\Delta H$ = 1, 2, 3 and 4 T for the sample $Pr_{0.58}Ho_{0.05}Sr_{0.37}MnO_3$

$\mu_0\Delta H$ (T)	T_C (K)	$-\Delta S_M^{max}$ ($J.kg^{-1}\cdot K^{-1}$)	δT_{FWHM} (K)	*RCP* ($J\cdot kg^{-1}$)
1	215	1.61	36	57.9
2	216	2.81	43	120.8
3	218	3.70	49	182.3
4	216	4.40	54	236.5

This behavior suggests the possibility of tuning the Curie temperature of the $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ compounds to cover the temperature range of the conventional domestic refrigerators by reducing the Ho ions concentration below x = 0.05, while the magnetic entropy change still maintains large values.

CONCLUSIONS

Magnetic properties and magnetocaloric effect in $Pr_{0.63-x}Ho_xSr_{0.37}MnO_3$ manganites (where x = 0; 0.01) were studied in detail. The compounds have ferromagnetic behavior below the Curie temperature. Replacing Pr^{3+} ions by Ho^{3+} ions results in a drastically reduction of the Curie temperature (T_C =215 K), while the magnetic entropy change and the relative cooling power still keep large values ($-\Delta S_M^{max}$ = 4.40 J/kg·K and *RCP* = 236 J/kg for ì$_0$ Ä*H* = 4 T) which recommend these compounds to be used in refrigeration applications in near room-temperature range.

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