

Magnetocaloric effect in $\text{La}_{1.2}\text{R}_{0.2}\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compounds

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Magnetocaloric effect of double layered manganites, $\text{La}_{1.4-x}\text{R}_x\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compounds where R = Nd, Sm, Ho or Yb were analysed. Polycrystalline samples were prepared by solid state reaction. Magnetic measurements were performed in magnetic fields up to 12 T and the temperature range 4.2-700 K. The Curie temperatures decrease with substitution. Above the Curie temperatures a small anomaly in the temperature dependences of the magnetization, around 250K was found. This phenomenon was explained by the presence of two dimensional short range magnetic order. The adiabatic magnetic entropy changes, $|\Delta S|$, were determined from magnetization data. Large MCE has been obtained in all samples. The potential use of these materials in magnetic refrigeration is discussed.

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1. Introduction

Magnetic materials showing a large magnetocaloric effect (MCE) have attracted considerable attention for their potential application in magnetic refrigeration technology [1-3]. MCE is an isothermal magnetic entropy change or an adiabatic temperature change of a magnetic material upon application of a magnetic field. The compounds which undergo temperature driven paramagnetic to ferromagnetic transitions show relatively large “negative” MCE, in which the isothermal magnetic entropy change is negative [4]. Refrigeration in the temperature range 250-300 K is of particular interest due to the potential impact on energy savings and environmental concerns.

In the last years many efforts were done in order to understand the interplay between structure, magnetic and transport properties in perovskite-type manganites. The substitution of the trivalent element by divalent one produce an inhomogeneous distribution of mixed valence $\text{Mn}^{4+}/\text{Mn}^{3+}$ ions to maintain charge neutrality. These systems exhibit many significant properties like charge and orbital ordering, metal-insulator transition, ferromagnetic-paramagnetic phase change, magnetoresistance, magnetocaloric effect, spin glass behaviour depending on the charge density, temperature and atomic structure [5-7]. Colossal magnetoresistance phenomena were observed in the perovskite-type hole-doped manganites in which the double-exchange ferromagnetic metal phase and the charge-orbital ordered antiferromagnetic phase compete with each other. The chemical randomness or the impurity doping may cause major modifications in the electronic phase diagram as well as in the magnetoelectronic properties. At present, the perovskite manganites are the most representative materials system which can show versatile unconventional electronic-lattice structural changes or insulator-metal transitions upon stimulation by

external stimuli, like magnetic field, irradiation with light, x-rays or electron-beams.

Compounds of the Ruddlesden - Popper (RP) series could be described generally as $(\text{RA})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ or $\text{AO}(\text{R}_{1-x}\text{A}_x\text{MnO}_3)_n$ [8]. The compounds with $n=\infty$ were intensively studied for their various magnetic and electric properties and colossal magnetoresistance effect. Several models have been proposed in order to explain the complex properties of these materials [9-12]. The models were based on the double exchange interaction conception, electron-lattice interaction caused by Jahn-Teller distortion, antiferromagnetic superexchange or charge-ordering interaction. The RP compounds with $n=2$ are bilayered perovskite and have quasi two dimensional crystal structure. These compounds are important for their inherent anisotropy and its consequences for studying low dimensional physics [13-17]. The double layered manganite consist of the ferromagnetic metallic MnO_2 bilayers separated by nonmagnetic $(\text{RCa})_2\text{O}_2$ insulating layers. These compounds exhibit very large magnetoresistance effect and two ferromagnetic transitions [15-22]. The set up of 2D ferromagnetic ordering at temperatures higher than 3D ferromagnetic ordering is a interesting feature of the double layered manganites [18-20]. During the last few years it was found that the perovskite manganites generate large magnetic entropy change under a moderate magnetic field [23,24].

In this paper we report the magnetocaloric effect in $\text{La}_{1.4-x}\text{R}_x\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compounds where R = Sm, Nd, Ho or Yb.

2. Experimental

Polycrystalline samples with nominal composition $\text{La}_{1.4-x}\text{R}_x\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compounds where R = Sm, Nd, Ho or Yb ($x = 0.0, 0.2$) were prepared by standard ceramic

reaction at high temperatures. The La_2O_3 , R_2O_3 and MnO_2 , were dried at 900°C for 6 hours. The mixtures of the respective oxides and CaCO_3 in stoichiometric proportions were calcinated at 900°C for 24 hour and then were pressed into pellets at 0.6 kbars and sintered in air at 900°C for 24 hours. For a better homogenization the samples were subsequently heated at 1200°C for 72 hours.

The powder X-ray diffraction patterns were recorded by using a Bruker D8 Advance AXS diffractometer with $\text{Cu K}\alpha$ radiation. An 12 T VSM from Cryogenics was used for magnetization measurements. The samples were studied

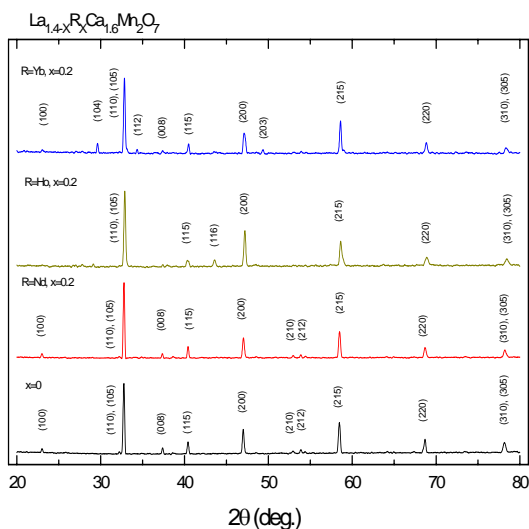


Fig.1. Diffraction patterns for $\text{La}_{1.4-x}\text{R}_x\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compounds.

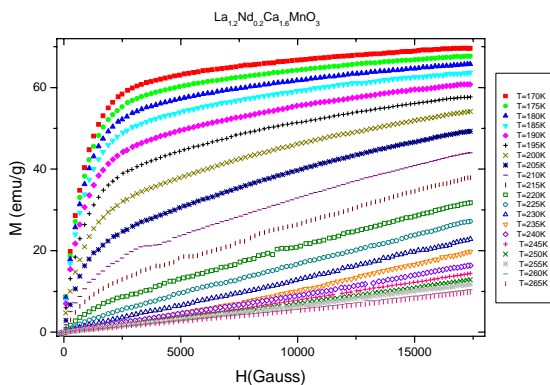


Fig.2. Magnetization isotherms for $\text{La}_{1.2}\text{Nd}_{0.2}\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compound.

in magnetic fields up to 12 T in the temperature ranges 4.2 – 700 K. The magnetic entropy changes were determined from magnetization isotherms, between zero

field and a maximum field (H_0) using the thermodynamic relation:

$$\begin{aligned} \Delta S_m(T, H_0) &= S_m(T, H_0) - S_m(T, 0) = \\ &= \frac{1}{\Delta T} \int_0^{H_0} [M(T + \Delta T, H) - M(T, H)] dH \end{aligned} \quad (1)$$

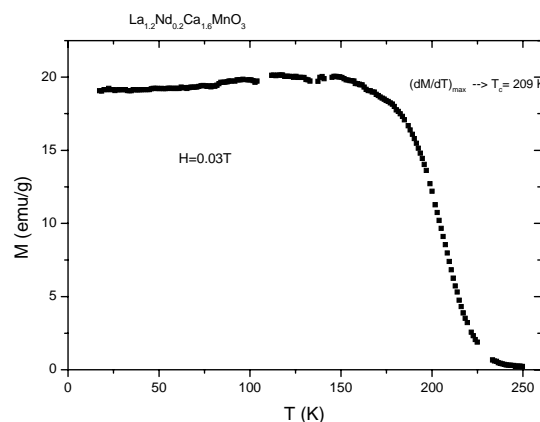


Fig. 3. The temperature dependences of the magnetization in a 0.03 T magnetic field for the compound with $x=0.2$ and $R=\text{Nd}$.

where ΔT is the temperature increment between measured magnetization isotherms. The magnetic cooling efficiency was evaluated by considering the magnitude of the magnetic entropy change, ΔS_m and its full-width at half-maximum (δT_{FWHM}). The product of the ΔS_m maximum and the ($\delta T_{\text{FWHM}}=T_2-T_1$):

$$\text{RCP(S)} = -\Delta S_m(T, H) \times \delta T_{\text{FWHM}} \quad (2)$$

is the so-called relative cooling power (RCP) based on the magnetic entropy change.

3. Results and discussions

The X-ray diffraction patterns for all the prepared samples showed mainly clean single phase compounds – see Fig. 1. The substitution of La^{3+} with R^{3+} ions does not affect the crystal structure. All the samples have tetragonal lattice structure of $\text{Sr}_3\text{Ti}_2\text{O}_7$ type. The lattice parameters show a small decrease when La is substituted by R atoms – see Table 1. The variation of lattice constants can be explained by the smaller ionic radius of R^{3+} as compared with La^{3+}

Table 1. Lattice parameters and Curie temperatures of $\text{La}_{1.4-x}\text{R}_x\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compounds.

x; R	x=0	0.2 Nd	0.2 Sm	0.2 Ho	0.2 Yb
a (Å)	3.864	3.861	3.859	3.852	3.856
c (Å)	3.856	19.24	19.24	19.235	19.24
T_C (K)	247.5	209	206	221	211

Some magnetization isotherms around the transition temperatures are presented in Fig. 2. The magnetization measurements do not show saturation for the studied samples. One can see that a transition from a ferromagnetic order to a paramagnetic one is present. The Curie temperatures were determined from Arrot plots and from the temperature dependences of the magnetization, in low field ($B=0.03$ T), at temperatures where dM/dT have minima. As example, in Fig.3. is presented the temperature dependence of the magnetization for the compound with $x=0.2$ and $R=\text{Nd}$ measured in external magnetic field of 0.03 T. The Curie temperatures determined by the two methods are quite the same, the difference being less than 1K. In Fig 4 are presented comparatively the temperature dependences of magnetizations for different samples.

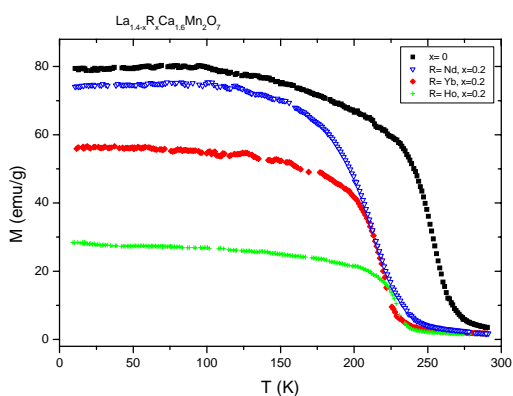


Fig.4. Temperature dependences of magnetizations for different samples in 1 T external magnetic field.

The Curie temperatures decrease when La is substituted by rare earths ions. The diminution of the Curie temperatures can be correlated with the structural changes. The R^{3+} radius are smaller as compared with La^{3+} one and induced a stronger structural distortion which has as result a tilting of the Mn-O-Mn angle and a diminution of the exchange interactions. It is important to pay attention to the temperatures region above the Curie temperatures where is still considerable magnetization until a small anomaly around 250 K in all cases. Similar behaviour was reported in Ref. [16,20,25,26].

This phenomena can be explained by the presence of a two dimensional (2D) short range magnetic order which still remain in the temperature range $T > T_C$ till the anomaly temperature, while the three dimensional (3D)

long range magnetic order disappear at the Curie temperature. Supplementary investigations are necessary in this temperature region.

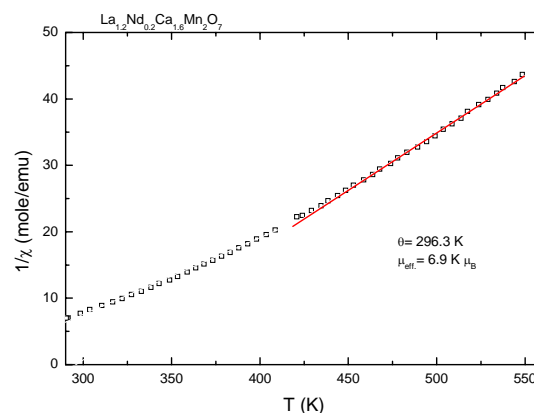


Fig.5. The temperature dependence of the reciprocal susceptibilities for the compound $\text{La}_{1.2}\text{Nd}_{0.2}\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compound.

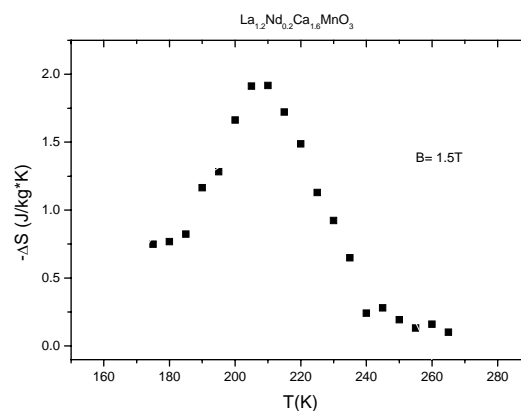


Fig. 6. Magnetic entropy changes around the transition temperature for the compound with Nd.

There are differences between the ZFC and FC curves, measured at low temperatures, showing a spin-glass like behaviour. The anisotropic spin glass state appears due to frustration of random competing double/exchange ferromagnetic and super-exchange antiferromagnetic interactions together with the anisotropy originating from layered structure. The competition of antiferromagnetic and ferromagnetic interactions can lead to the frustration, which is responsible for spin glass-like (cluster glass) behavior observed in some perovskite manganites and cobaltites.

The temperature dependence of the reciprocal susceptibility, above the Curie temperature, for the compound with $R=\text{Nd}$ is presented in Fig 5. At

temperatures below 400 K the temperature dependence of the reciprocal susceptibility is not linear, probable due to appearance of clusters. From the linear portions of the curve the Curie constant was determined and from this value the effective magnetic moments per formula unit was calculated. Considering that the contribution of Nd atoms to the effective magnetic moment is the same like of the free Nd^{3+} ion the effective magnetic moment per Mn atom was determined. It obtained value was $4.74 \mu_B/\text{Mn}$ atom. Considering that there exist a mixture of Mn^{3+} and Mn^{4+} ions their relative concentration was calculated. It were found that 18% of ions are Mn^{4+} and 82% are Mn^{3+} , that mean a average valence of +3.34 for Mn. Considering the neutrality charge condition for the stoichiometric compound 30% are Mn^{4+} and 70 % are Mn^{3+} . The average Mn valence is +3.30. A possible explanation for this difference between Mn average valences could be explained through the presence of more oxygen (7.04 instead of 7) on formula unit, the difference being chemical absorbed oxygen [27].

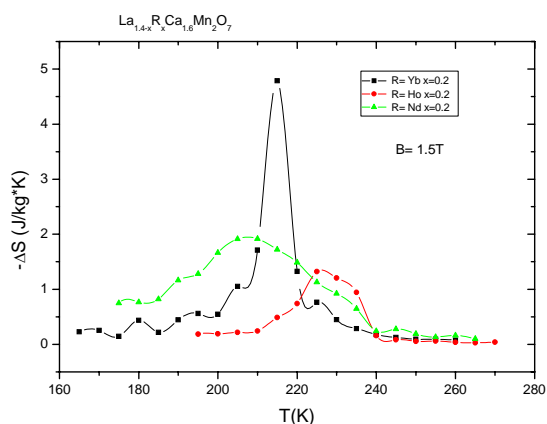


Fig.7. Comparison of the magnetic entropy changes around transition temperatures for the compounds with $R=\text{Nd, Ho, Yb}$.

The temperature dependences of the magnetic entropy changes, around transition temperatures, in magnetic fields of 1.5 for the compound with $R=\text{Nd}$ are plotted in Fig.6. In Fig.7 are presented comparatively the temperature dependence of the magnetic entropy change for different compound from the series. The maximum values of $|\Delta S|$ are at temperatures very close to the magnetic transition ones. One can see that the curves are almost symmetrical at two sides of their peak value. In general this phenomenon is characteristic of a second order magnetic transition [28]. The peaks broadened out above Curie temperatures. The broadening of the magnetic entropy change can be interpreted by the 2D short-range magnetic order which is still present. The maximum values are 2.85 J/kgK for the compound with $x=0$; 2.4 J/kgK for the compound with $R=\text{Nd}$, 2.3 J/kgK for $R=\text{Sm}$, 2.1 J/kgK for $R=\text{Yb}$ and 1.87 J/kgK for the compound with Ho in 2T

magnetic field. The determined ΔS values are rather high for compounds showing a second order type transition. The decrease of the magnetic entropy change with composition can be attributed to the diminution of the exchange interactions. The RCP(S) values are 85.5 J/kg ($x=0$), 78.5 J/kg ($R=\text{Nd}$) 71.4 J/kg ($R=\text{Sm}$) 58.8 J/kg ($R=\text{Yb}$) and 44.88 J/kg ($R=\text{Ho}$) obtained in 2T magnetic field. This value decrease to 16.32 J/kg for $x=0$ sample in 0.5 T magnetic field. The obtained RCP(S) values are comparable with that obtained in other compounds. In conclusion these compounds are promising materials for technical applications. Another advantage of these materials for the magnetic refrigeration is the broadening of the magnetic entropy peaks and the easiest way to tune the transition temperature.

4. Conclusions

The structure, magnetic properties and the magnetic entropy change of $\text{La}_{1.4-x}\text{R}_x\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compounds where $R = \text{Nd, Sm, Ho}$ or Yb have been investigated. The substitution of R atoms for La does not affect the crystal structure but it leads to a small decrease of the lattice parameters. The Curie temperatures decrease when La is substituted by R atoms.

The decrease of the Curie temperatures can be correlated with the structural changes. The R^{3+} radius are smaller as compared with La^{3+} one and induced a stronger structural distortion which has as result a tilting of the Mn-O-Mn angle and a diminution of the exchange interactions.

The anomalous magnetization plateau above the Curie temperature can be explained by the presence of a two dimensional (2D) short range magnetic order.

The anisotropic spin glass state confirmed by ZFC and FC measurements appears due to frustration of random competing double/exchange ferromagnetic and super-exchange antiferromagnetic interactions together with the anisotropy originating from layered structure. Probably a small excess of oxygen is present as was found from magnetic measurements in paramagnetic region.

The maximum values of the magnetic entropy change are at temperatures very close to the magnetic transition ones. The maximum value was obtained for the $\text{La}_{1.4}\text{Ca}_{1.6}\text{Mn}_2\text{O}_7$ compound being 2.85 J/kgK in 2T magnetic field. The magnetic entropy change vs temperature curves are almost symmetrical at two sides of their peak value, this phenomenon being characteristic of a second order magnetic transition. The decrease of the magnetic entropy change with composition can be attributed to the decrease of the exchange interactions due to substitutions.

The obtained RCP(S) values are comparable with that obtained in other compounds. These RCP(S) values together with the broadening of the magnetic entropy peaks and the possibility to tune the transition temperature show the advantages of these materials for the magnetic refrigeration.

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