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Magnetic properties and magnetocaloric effect in $La_{1.4-X}R_XCa_{1.6}Mn_2O_7$ compounds with R=Ho or Yb

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Magnetic properties and magnetocaloric effect (MCE) of double layered manganites, $La_{1.4-X}R_XCa_{1.6}Mn_2O_7$, where R = Ho or Yb and x=0 or 0.2 were analysed. Polycrystalline samples were prepared by solid state reaction. Magnetic measurements were performed in magnetic fields up to 5 T in the temperature range 4.2-300 K. The Curie temperatures decrease from 246 K (x=0) to 211 K (x=0.2) for R=Yb and 221 K (x=0.2) for R=Ho. Above the Curie temperatures small anomalies in the temperature dependences of the magnetizations were found. These were 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 shown in all samples. The potential use of these materials for magnetic refrigeration is discussed.

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Keywords: Manganites, Magnetocaloric effect, Magnetization

1. Introduction

Compounds of the Ruddlesden - Popper (RP) series could be described generally as $(RA)_{n+1}Mn_nO_{3n+1}$ or $AO(R_{1-x}A_xMnO_3)_n$ where R is a rare earth and A an alkali earth metal [1]. The compounds with n=∞ were intensively studied for their interesting magnetic, electrical properties and colossal magnetoresistance effects. Several models have been proposed in order to explain the compex properties of these materials [2-5]. The models were based on the double exchange interaction concept, electron-lattice interaction caused by Jahn-Teller distorsion, antiferomagnetic superexchange or charge-ordering mechanism. The RP compounds with n=2 are bilayered perovskite and have quasi-two dimensional crystal structure. These compounds are important for their resulting anisotropy and its interest for low dimensional physics [6-10]. The double layered manganites consist of the ferromagnetic metallic MnO_2 bilayers separated by nonmagnetic $(RCa)_2O_2$ insulating layers. These compounds exhibit very large magnetoresistance and two ferromagnetic transitions [8-15]. The set up of 2D magnetic ordering at temperatures higher than 3D magnetic ordering, is a interesting feature of the double layered manganites [11-13].

During the last few years it was found that the perovskite manganites generate large magnetic entropy change under a moderate magnetic field [16,17]. Magnetic materials showing a large magnetocaloric effect (MCE) have attracted considerable attention for their potential application in magnetic refrigeration technology [18-20]. 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 paramagnetic to magnetic ordered transitions show relatively large "negative" MCE, in which the isothermal magnetic entropy change, is negative [21]. Refrigeration in the temperature range 250-300 K is of particular interest due to the potential impact on energy savings and environmental concerns.

The interplay between structure, magnetic and transport properties in perovskite-type manganites was the aim of many recent papers. The substitution of the trivalent element by divalent one produce an inhomogeneous distribution of mixed valence Mn^{4+}/Mn^{3+} ions to maintain charge neutrality. The chemical randomness or the impurity doping may cause major modifications in the electronic phase diagram as well as in the magnetoelectronic properties.

In this paper we report the magnetic properties and magnetocaloric effect in $La_{1.4-X}R_XCa_{1.6}Mn_2O_7$ compounds where R = Ho or Yb.

2. Experimental

Polycrystalline samples with nominal composition $La_{1.4-X}R_XCa_{1.6}Mn_2O_7$, where R = Ho or Yb ($x$ = 0.0, 0.2) were prepared by standard ceramic reaction at high temperatures. The La_2O_3, Ho_2O_3 and Yb_2O_3, 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 Cu Kα radiation. An Oxford Instruments MagLab System

2000 was used for magnetization measurements. The samples

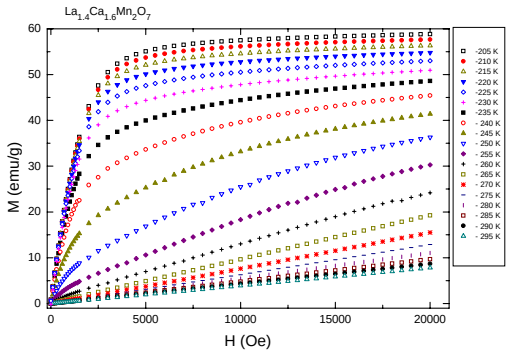

Fig. 1. Magnetization isotherms for $La_{1.4}Ca_{1.6}Mn_2O_7$ compound.

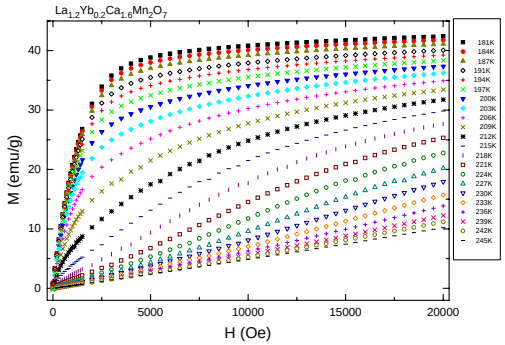

Fig. 2. Magnetization isotherms for $La_{1.2}Yb_{0.2}Ca_{1.6}Mn_2O_7$ compound.

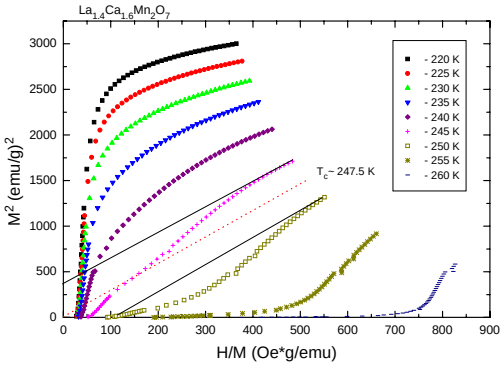

Fig. 3. Arrott plots for the compound with x=0.

were studied in magnetic fields up to 5 T, in the temperature ranges 4.2 - 750 K. The magnetic entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation:

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

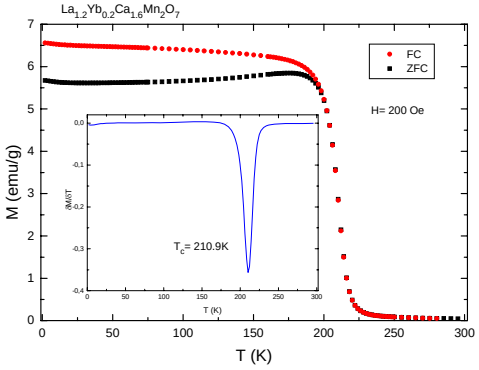

Fig. 4. The temperature dependences of the ZFC and FC magnetizations in a 0.02 T field for the compound with x=0.2 and R=Yb. In inset the dM/dT values are also given.

where ΔT is the temperature increment between measured magnetization isotherms (ΔT = 5K for the compound with x=0 and ΔT = 3 K for the compounds with Ho and Yb). 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 ($\delta T_{FWHM}=T_2-T_1$):

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

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

3. Results and discussion

The X-ray diffraction patterns for all the prepared samples showed the presence of single phase compounds. The samples have orthorombic lattice of $Sr_3Ti_2O_7$ type. The lattice parameters decrease when La is substitutted by Ho or Yb – see Table 1. The variation of lattice constants can be explained by the smaller ionic radius of Ho^{3+} and Yb^{3+} as compared with La^{3+}.

Table 1. Lattice parameters and Curie temperatures of $La_{1.4-x}R_xCa_{1.6}Mn_2O_7$ compounds.

x; R	x=0	x=0.2; R=Ho	x=0.2; R=Yb
a (Å)	3.864	3.852	3.856
c (Å)	19.24	19.235	19.24
T_C (K)	247.5	221	211

Some magnetization isotherms around the transition temperatures are presented in Fig. 1 and Fig. 2. One can see that a transition from a magnetic order state to a paramagnetic one is present below room temperature. The Curie temperatures were determined from Arrott plots and from the temperature dependences of the magnetization, in low field (B=0.02 T), at temperatures where dM/dT have minima. As example in Fig. 3. are presented the Arrott

plots for the compound with x=0. The temperature dependences of the magnetizations for FC and ZFC $La_{1.2}Yb_{0.2}Ca_{1.6}Mn_2O_7$ in field of 200 Oe are plotted Fig. 4. The Curie temperatures determined from Arrott plots and from M vs. T are the same. The T_C values decrease when La is substituted by Ho or Yb. The diminuation of the Curie temperatures can be correlated with the structural changes. The Ho^{3+} and Yb^{3+} radius are smaller as compared with La^{3+} one and induced a stronger structural distorsion which result in a tilting of the Mn-O-Mn angle and a diminution of the exchange interactions strenght. It is important to pay attention to the $T > T_C$ region where it is still considerable magnetization untill a small anomaly around 250 K. Similar behaviour was reported previously [9,13,18]. This phenomena can be explained by the presence of a two dimensional (2D) short range magnetic order which still remain at $T > T_C$ while the three dimensional (3D) long range magnetic order dissapear at the Curie temperature.

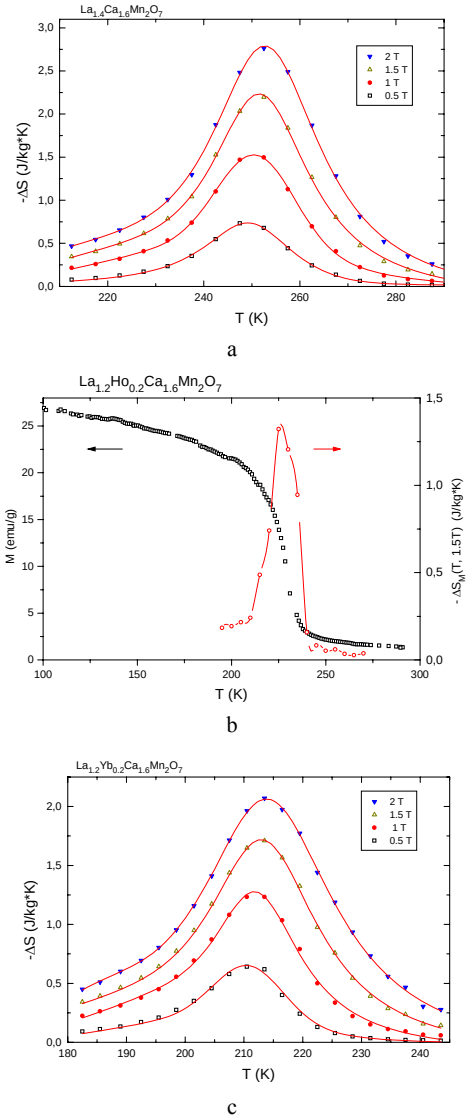

Fig. 4. Magnetic entropy changes around transition temperatures.

There are differences between the ZFC and FC curves, measured at low temperatures, showing a spin-glass like behaviour. The spin glass state appears due to frustration of random competing ferromagnetic double exchange, super-exchange and antiferromagnetic interactions together with the anisotropy originating from layered structure.

The temperature dependences of the magnetic entropy changes, around transition temperatures, in magnetic fields of 0.5; 1.0; 1.5 and 2.0 T for compounds with x=0 and x=0.2 (R= Ho and Yb) are plotted in Fig.4. The maximum values of $|\Delta S|$ are located at temperatures very close to the magnetic transition ones. One can see that the ΔS vs T curves in Fig. 4. are nearly symmetrical around their peak values. In general this phenomenon is characteristic of a second order magnetic transition [19]. The small broadening of the magnetic entropy change at $T > T_C$ curve, as compared to one obtained at $T < T_C$ can be attributed to the 2D short-range magnetic order which is still present. The maximum in $|\Delta S|$ values are 2.85 J/kgK for the compound with x=0; 2.1 J/kgK for the compound with Yb and 1.87 J/kgK for the compound with Ho in 2T magnetic field. The determined ΔS values are rather high for systems 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 of 85.5 J/kg (x=0), 58.8 J/kg (x=0.2; R=Yb) and 44.88 J/kg (x=0.2; R=Ho) were obtained in 2T magnetic field. These values decrease to 16.32 J/kg for $La_{1.4}Ca_{1.6}Mn_2O_7$ sample in 0.5 T magnetic field. The RCP(S) values are comparable with those obtained in other oxide compounds. In conclusion these compounds are promising materials for technical apllications. Another advantage of these materials for the magnetic refrigeration is the broadening of the magnetic entropy peaks.

4. Conclusions

The structure, magnetic properties and the magnetic entropy change of $La_{1.4-X}R_XCa_{1.6}Mn_2O_7$ compounds where R = Ho or Yb and x=0 and 0.2 have been investigated. The substitution of Ho or Yb 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 Ho or Yb. The diminuation of the Curie temperatures can be correlated with the structural changes. The Ho^{3+} and Yb^{3+} radius are smaller as compared with La^{3+} one and induced a structural distorsion which have 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 spin glass state was confirmed by ZFC and FC measurements. This appears due to frustration of random competing double/exchange ferromagnetic and super-

exchange antiferromagnetic interactions together with the anisotropy originating from layered structure.

The peaks of the magnetic entropy change are located at temperatures very close to the magnetic transition ones. The maximum value of 2.85 J/kgK was obtained for the $La_{1.4}Ca_{1.6}Mn_2O_7$ compound in 2T magnetic field. The magnetic entropy change vs temperature curves are almost symmetrical around their peak values, this phenomenon being characteristic of a second order magnetic transition. The decrease of the magnetic entropy change can be attributed to the diminution of the exchange interactions as result of substitutions.

The RCP(S) values (85.5 J/kg for the sample with x=0) are comparable with that obtained in other oxide compounds. These RCP(S) values together with the broadened magnetic entropy curves suggest the possibility to use these materials for the magnetic refrigeration devices.

Acknowledgments

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