STUDIA UBB PHYSICA, Vol. 67 (LXVII), 1-2, 2022, pp. 9-16
(RECOMMENDED CITATION)
doi:10.24193/subbphys.2022.01

MAGNETOCALORIC EFFECT IN $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ (R=Tb, Dy, Ho, Er) PEROVSKITES SYNTHESIZED BY SOL-GEL METHOD

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ABSTRACT. Nanocrystalline double layered $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ manganites with R = Tb, Dy, Ho, and Er were synthesized by sol-gel method. The XRD measurements indicate that all samples are single phase with a $Sr_3Ti_2O_7$-type tetragonal (I4*/mmm*) structure and mean crystallite sizes between 22 nm and 27 nm. The magnetic measurements evidence a spin-glass like behavior at low temperatures for all samples, which may be due to frustration of random competing ferromagnetic and antiferromagnetic interactions together with the anisotropy originating from the layered structure. A moderate magnetocaloric effect was found for all samples, with the maximum entropy change located at temperatures near the magnetic transition ones, but high *RCP*(*S*) values were obtained due to the broadened magnetic entropy curves.

Keywords: *nanoparticles, double layered perovskite, magnetocaloric effect.*

INTRODUCTION

The double-layered manganites show many intriguing properties such as colossal magnetoresistance, charge ordering, anisotropic transport in charge carriers, and the possibility of a short-range magnetic ordering above the 3D ferromagnetic transition temperature [1-7]. The doped $R_{2-2x}A_{1+2x}Mn_2O_7$ perovskites (R is a trivalent rare earth ion and A is a divalent alkaline earth cation) consist of MnO_2 bilayers separated by insulating $(R,A)_2O_2$ rock-salt layers, stacked along the *c*-axis, leading to a quasi-two-dimensional structure. The inherent anisotropy

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resulted from their layered structure and its consequences for studying low-dimensional physics, as well as the remarkable range of physical properties have generated much interest. Two anisotropic exchange interactions are expected in these manganites, namely: an intralayer exchange interaction within the MnO_2 bilayers and an interlayer exchange interaction acting between the perovskite MnO_2 bilayers, which could be the reason for the two transition temperatures for magnetic ordering [2,8,9]. Among other intriguing properties, $La_{2-2x}Ca_{1+2x}Mn_2O_7$ perovskites exhibit colossal magnetoresistance (CMR) effect at low temperatures [1,3,10] and large magnetic entropy change under a moderate magnetic field [11-13].

The physical properties of double-layered manganites are sensitive to small changes in composition and structure [4]. In particular, the magnetic transition Curie temperature and the magnetic entropy change are influenced by the preparation conditions of these materials. The substitution of La with other rare earth atoms may induce lattice effects and/or change the magnetic interactions.

In this work we present the magnetic properties and magnetocaloric effect of $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ with R = Tb, Dy, Ho, and Er manganites.

EXPERIMENTAL

Polycrystalline powders of $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ with R = Tb, Dy, Ho, and Er perovskites were synthesized by sol-gel method, as previously described [14].

The crystal structure of the samples was analyzed at room temperature by using a Bruker D8 Advance AXS X-ray diffractometer with Cu *Kα* radiation in the 2θ region 20°-90°. The crystallite-sizes of the powders were estimated according to the Debye-Scherrer equation:

$$D = \frac{\mathrm{k}\lambda}{\beta \cos\theta} \tag{1}$$

where *β* is the peak full width at half maximum (in radians) at the observed peak angle *ϑ*, k is the crystallite shape factor (was considered 0.94) and λ is the X-ray wavelength (0.154 nm).

Magnetic measurements were carried out on pellets, obtained from pressing the powders, using a 12 T VSM from Cryogenics in the temperature range 4.2 – 300 K. The magnetic entropy changes were determined from magnetization isotherms, between zero field and a maximum field (H_0) using the thermodynamic relation:

$$\Delta S_m(T,H_0) = S_m(T,H_0) - S_m(T,0) = \frac{1}{\Delta T}\int_0^H [M(T+\Delta T,H) - M(T,H)]dT \tag{2}$$

where ΔT = 5 K is the temperature increment between measured magnetization isotherms. The magnetic cooling efficiency was evaluated by calculating the relative cooling power (RCP) based on the magnetic entropy change:

$$RCP(S) = -\Delta S_m(T, H_0) \times \delta T_{FWHM} \tag{3}$$

ΔS_m represents the maximum magnetic entropy change and δT_{FWHM} its full-width at half-maximum.

RESULTS AND DISCUSSION

The crystal structure and crystallite sizes of the polycrystalline powders obtained by sol-gel method were determined by Rietveld refinement of XRD patterns using FullProf Suite Software [15]. The X-ray diffraction analysis (Fig. 1) shows that all $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ are single phase with a $Sr_3Ti_2O_7$-type tetragonal (I4/*mmm*) structure.

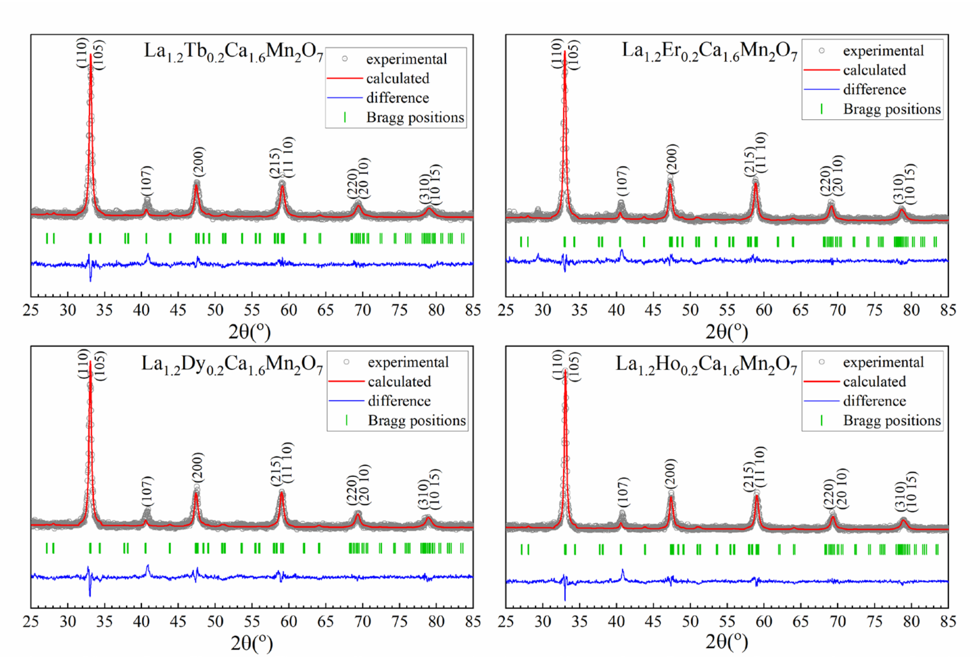

Fig. 1. Rietveld refinement results for the XRD patterns of $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ manganites recorded at room temperature.

The lattice parameters calculated using the Rietveld method, *c/a* ratios and crystallite-sizes obtained using the Debye-Scherrer equation are collected in Table 1. The lattice parameters determined for $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ are smaller than for $La_{1.4}Ca_{1.6}Mn_2O_7$ (c = 19.176(6) Å, c/a = 4.988) [14], which is expected considering the smaller ionic radius of Tb, Dy, Ho, or Er as compared to La. The slight decrease of *c/a* ratio suggests that the lattice contracts preferably in the *c*-direction rather than in the *a*-direction when La is substituted by other rare earth ions, as previously found for Ce, Pr, Nd, Sm, Gd [14,16,17]. For all samples the mean crystallite size was found to be around 25 nm.

Table 1. Lattice parameters, *c/a* ratio and crystallite sizes estimated from XRD patterns

	a (Å)	*c* (Å)	*c/a*	Crystallite size (nm)
$La_{1.2}Tb_{0.2}Ca_{1.6}Mn_2O_7$	3.835(6)	19.050(0)	4.966(6)	22±1
$La_{1.2}Dy_{0.2}Ca_{1.6}Mn_2O_7$	3.838(9)	19.100(9)	4.975(6)	23±1
$La_{1.2}Ho_{0.2}Ca_{1.6}Mn_2O_7$	3.839(2)	19.094(7)	4.973(6)	27±1
$La_{1.2}Er_{0.2}Ca_{1.6}Mn_2O_7$	3.848(7)	19.141(4)	4.973(4)	24±1

The magnetic properties of $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ with R = Tb, Dy, Ho, and Er perovskites were studied by analyzing the temperature dependence of the zero field cooling (ZFC) and field cooling (FC) magnetizations under a magnetic field of 0.2 T (Fig. 2).

The curves presented in Fig. 2 show a wide ferromagnetic transition, change in slope in the temperature range of 50 – 200 K. The Curie temperature, defined as the temperature corresponding to the maximum of $|\delta M/\delta T|$, is in the range 70 K to 80 K for all samples, as it can be seen in the insets of Fig. 2. The wide ferromagnetic transition in double layered manganites is due to the appearance of short range 2D-magnetic order at temperatures higher than the 3D-ferromagnetic transition temperature [1,18], which is also responsible for the non zero magnetization value at room temperature. For all investigated perovskites, a clear splitting between the ZFC and FC magnetizations can be observed at low temperatures with a maximum of the ZFC curve at about 35 K. The difference between the FC and ZFC curves can be explained by the surface driven spin frustration and disorder in nanoparticles [19-21] together with the anisotropy originating from layered structure. This is supported by the reduced values of the magnetization at 5 K, that do not reach saturation even in magnetic fields of 12 T, as shown in Fig. 3 for $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ with R = Tb, Dy, Ho, and Er. Also, the M(H) curves presented in Fig. 4 exhibit clear hysteresis at 5 K, which is diminishing with increasing temperature and is almost absent at 75 K.

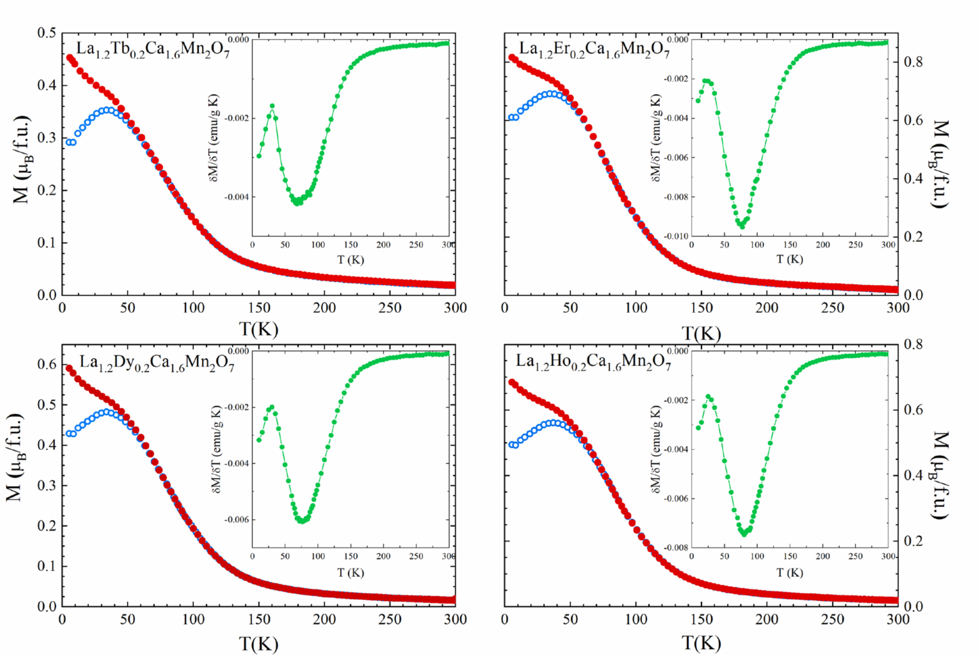

Fig. 2. Temperature dependence of ZFC (open symbols) and FC (filled symbols) magnetizations in 0.2T.

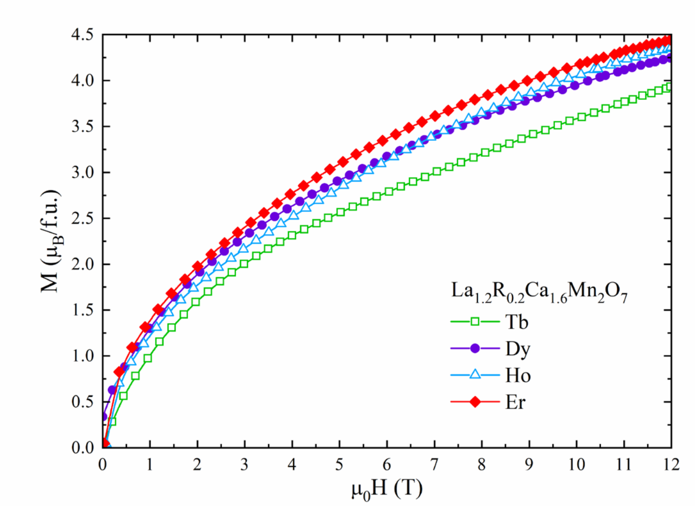

Fig. 3. *M(H)* curves at 5 K in magnetic fields up to 12 T.

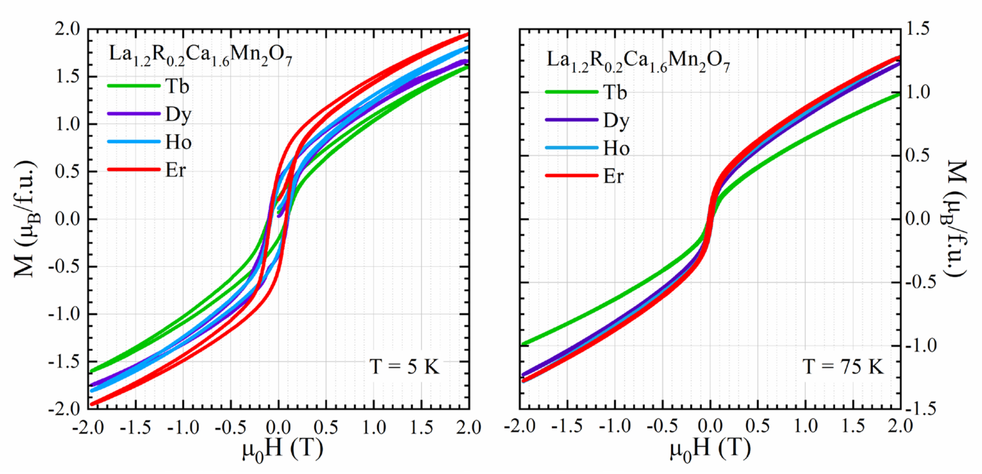

Fig. 4. Magnetic field dependence of the magnetization at 5 K (left) and 75 K (right).

Fig. 5 shows the temperature dependences of the magnetic entropy changes induced by a magnetic field change of 4 T for $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ with R = Tb, Dy, Ho, and Er, as determined from magnetization isotherms using equation 2. For all samples the magnetic entropy change has a significant value over a broad temperature range, with a maximum at temperatures close to the magnetic transition ones.

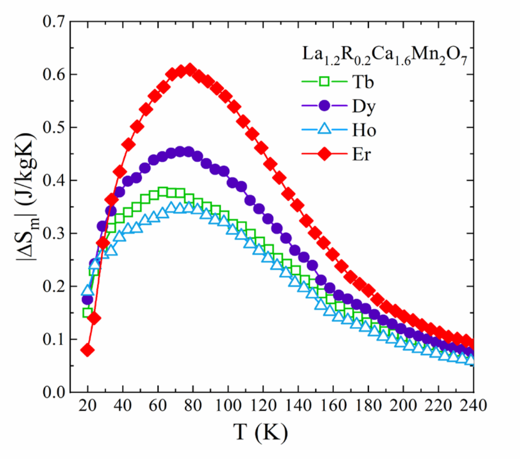

Fig. 5. Temperature dependence of the magnetic entropy changes ΔS_m for ΔH = 4 T.

The magnetocaloric properties of the investigated samples, including the *RCP(S)* values calculated by using equation 3, are presented in Table 2. The maximum values of $|\Delta S_m|$ are rather small since the magnetization of the samples in 4 T is far from the saturation value, but the *RCP(S)* values are high due to the broadened magnetic entropy curves.

Table 2. Magnetocaloric properties of $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ perovskites

	T_C (K)	T_{max} (K)	$\lvert\Delta S_{Max}\rvert$ (J/KgK)	δT_{FWHM} (K)	*RCP(S)* (J/kg)
$La_{1.2}Tb_{0.2}Ca_{1.6}Mn_2O_7$	72±1	67±1	0.38±0.01	131±1	50±1
$La_{1.2}Dy_{0.2}Ca_{1.6}Mn_2O_7$	76±1	71±1	0.45±0.01	127±1	57±1
$La_{1.2}Ho_{0.2}Ca_{1.6}Mn_2O_7$	80±1	73±1	0.35±0.01	131±1	46±1
$La_{1.2}Er_{0.2}Ca_{1.6}Mn_2O_7$	77±1	76±1	0.61±0.01	118±1	72±1

CONCLUSIONS

Nanocrystalline $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ with R = Tb, Dy, Ho, Er double layered manganites were successfully synthesized by a direct sol-gel method. The XRD analysis reveals that the partial substitution of La with smaller ions does not change the crystal structure and that the lattice contracts preferably in the *c*-direction rather than in the *a*-direction. The increased inter-layer lattice distortion leads to the reduction of the exchange interaction strength. The magnetic measurements show clear differences between FC and ZFC magnetizations at low temperatures for all four samples, which may be due to frustration of random competing ferromagnetic and antiferromagnetic interactions together with the anisotropy originating from layered structure. The magnetization at 4 K of $La_{1.2}R_{0.2}Ca_{1.6}Mn_2O_7$ manganites with R = Tb, Dy, Ho, Er does not saturate even in magnetic fields of 12 T. This may be due to the absence of true long-range FM coupling in the nanocrystalline samples obtained by the sol-gel method for which the grain size is smaller than 30 nm. A moderate magnetocaloric effect was found for all samples, with the maximum entropy change located at temperatures near the magnetic transition ones. The high *RCP(S)* values together with the broadened magnetic entropy curves and the absence of magnetic hysteresis at temperature higher than 50 K suggest the possibility to use these materials for magnetic refrigeration devices.

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