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Magnetic, transport, and magnetocaloric properties of double perovskite oxide $LaCaMnCoO_6$

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Magnetic, magnetoresistive, and magnetocaloric properties of a novel double perovskite oxide, namely, $LaCaMnCoO_6$ have been studied. Polycrystalline sample of $LaCaMnCoO_6$ has been synthesized by sol-gel technique. It has cubic crystal structure (space group $Fm\bar{3}m$) at room temperature. The temperature variation in magnetization reveals a steep increase in magnetization around 168 K (T_C). The magnetization does not even saturate at 5 K and a magnetic moment of $0.7\mu_B$/f.u. is obtained at 5 K in an applied field of 50 kOe. The electrical resistivity measurement indicates that the material is semiconducting-like in the temperature range of ~300–50 K and below ~50 K the sample becomes insulating. A maximum magnetoresistance (MR) of about 8% is found at 200 K in an applied field of 7 T and MR has a negative sign. The magnetocaloric effect is calculated from the magnetization versus temperature data and a maximum magnetic entropy change of 3.1 J/kg K for a field change of 11 kOe is obtained near T_C. Thus a moderate magnetocaloric effect is achieved in rather low magnetic fields. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3059592]

INTRODUCTION

Double perovskite oxides of general formula $AA'BB'O_6$ (A,A'—rare earth or alkaline earth ions and B,B'—transition metal ions) have recently received great attention because some of them exhibit colossal magnetoresistance and half-metallic nature with coexisting ferro-ferrimagnetism. These compounds are known for decades.[1–6] These compounds often show large magnetocaloric effect (MCE) near the second order transition temperature T_C.[7,8] The MCE refers to the capacity of magnetic materials to change their temperature under the application or the removal of an external magnetic field. The use of the MCE for building magnetic refrigerators appears as a good alternative to the classical refrigeration systems based on a compression/expansion vapor cycle because it is an environmental friendly technology and also suitable for reducing energy costs.[9] In the present work we report magnetic, magnetoresistive, and magnetocaloric properties of a novel double perovskite oxide, namely, $LaCaMnCoO_6$. The compound is found to show semiconducting-like behavior with a cubic double perovskite structures and exhibits ferrimagnetic behavior.

EXPERIMENTAL DETAILS

Polycrystalline sample of $LaCaMnCoO_6$ was prepared by the sol-gel method using stoichiometric mixtures of high purity La_2O_3, $CaCO_3$, $Mn(CH_3COO)_2$, and $CoCl_2 \cdot 6H_2O$. These were first dissolved in water and then appropriate amounts of citric acid was added to the solution. The gel formation was catalyzed by the addition of nitric acid. The resulted gel was decomposed at 120 °C and then acquired precursor powders were heated in air first at 800 °C for 12 h and 1000 °C for 12 h duration. The sample was characterized by x-ray powder diffraction (XRD) using PANalytical X'pert diffractometer with Cu $K\alpha$ radiation. The energy dispersive x-ray analysis was performed using a scanning electron microscope (Philips FEI QUANTA 200). Dc magnetization of the sample was measured using a superconducting quantum interference device magnetometer (magnetic property measurement system, Quantum Design). Magnetization at various fields has been measured using a vibrating sample magnetometer in fields up to 12 kOe. Electrical resistivity has been measured on a bar shaped pellet by standard four probe method using physical property measurement system (Quantum Design) in the presence of various applied magnetic fields.

RESULTS AND DISCUSSION

The Rietveld refinement for the compound $LaCaMnCoO_6$ was carried out using the GSAS package.[10] The goodness of the fit, refined lattice parameter, and atomic positions were given in Table I. The observed, calculated, and difference XRD profiles of the compound are shown in Fig. 1. The single phase nature of the compound was confirmed by the Rietveld analysis. The obtained unit cell parameter of 7.650 Å was slightly lower compared to the compound $LaSrMnCoO_6$,[11] which is in agreement with the fact that ionic radius of Ca^{2+} is smaller then that of Sr^{2+} ion. The temperature dependence of magnetization, $M(T)$, measured in applied field of 5 kOe is shown in Fig. 2. The temperature

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TABLE I. Crystal data for structure refinement for compound $LaCaMnCoO_6$.

Crystal system, space group	Cubic, $Fm\bar{3}m$		
Unit cell dimensions	$a=b=c=7.650$ Å		
Volume	447.763 (Å^3)		
2θ range for data collections	10°–110°		
R_{wp}	4.54%		
R_p	3.2%		
χ^2	1.877		
Atom	x	y	z
La	1/4	1/4	1/4
Ca	1/4	1/4	1/4
Mn	1/2	0	0
Co	0	0	0
O	0.2492	0	0

dependence of inverse molar susceptibility, $\chi^{-1}(T)$, is plotted and is shown as an inset in Fig. 2. The shape of the $\chi^{-1}(T)$ curve suggests that the sample displays ferrimagnetic behavior. In the temperature range between 200 and 300 K, the $\chi^{-1}(T)$ data fit well with the Curie–Weiss law. The experimental value for the paramagnetic Curie temperature is $\theta=77$ K and the effective magnetic moment is $p_{\text{eff}}=6.28\mu_B$. The value of p_{eff} suggests that the oxidation states of manganese and cobalt are Mn^{4+} ($S=3/2$) and Co^{3+} ($S=2$) since the spin only moment for $LaCaMnCoO_6$ is calculated to be $6.31\mu_B$. The dc magnetization as a function of an applied magnetic field measured at $T=5$ K shows a small hysteresis in the M-H curve, consistent with the ferrimagnetic behavior mentioned above. Also the magnetization remains unsaturated even under the applied field of 50 kOe. The magnetization value of $0.7\mu_B$/f.u. is obtained at 5 K in an applied field of 50 kOe.

The temperature dependence of the electrical resistivity of $LaCaMnCoO_6$ is shown in Fig. 3, which indicates that this compound is semiconducting-like behavior in the temperature range of 300–50 K and below ~50 K the sample becomes insulating. The $\ln\rho$ versus $1/T^{1/4}$ plot (shown in inset of Fig. 3) is linear, indicating a variable range hopping (VRH) of charge carriers. A maximum negative magnetoresistance of about 8% is found at 200 K in an applied field of 7 T. Based on thermodynamic theory, the entropy change (which results from the spin ordering and is induced by the variation of the applied magnetic field from 0 to $H_{\max}$) is given by[12]

$$|\Delta S_M| = \int_0^{H_{\max}} \left(\frac{\partial M}{\partial T}\right) dH. \quad (1)$$

According to Eq. (1), the magnetic entropy change ($|\Delta S_M|$) depends on the temperature gradient of the magnetization and attains a maximum value around the Curie temperature, at which the magnetization decays most rapidly. In Fig. 4, we show the temperature dependence of magnetic entropy change $|\Delta S_M|$ for a field variation of 11 kOe for $LaCaMnCoO_6$. Upon 11 kOe applied field change, the maximum $|\Delta S_M|$ of ~3.1 J/kg K is obtained for $LaCaMnCoO_6$ compound. This value is moderate when compared to the maximum magnetic entropy change of ~4.2 J/kg K realized in elemental Gd for a field change of 1.5 T near its magnetic ordering temperature, 294 K.[13]

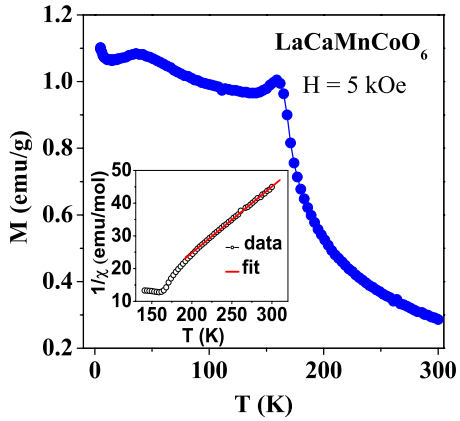

FIG. 2. (Color online) Temperature dependence of magnetization of $LaCaMnCoO_6$ measured in a magnetic field of 5 kOe. Inset shows inverse magnetic susceptibility and fit to Curie–Weiss law.

CONCLUSION

The double perovskite oxide $LaCaMnCoO_6$ prepared by sol-gel method and it is found to have cubic structure at room temperature. The sample undergoes a magnetic transition around 168 K. The resistivity data show that the com-

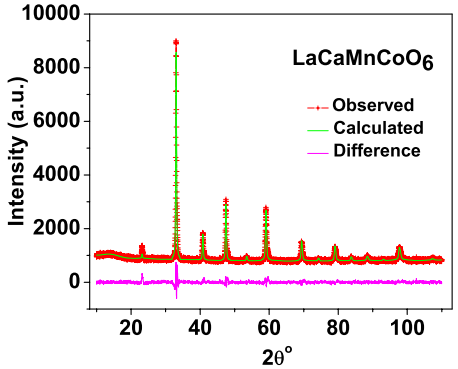

FIG. 1. (Color online) Powder x-ray diffraction pattern of $LaCaMnCoO_6$ measured at room temperature (crosses). The solid line is the calculated profile and difference is plotted at the bottom of the figure.

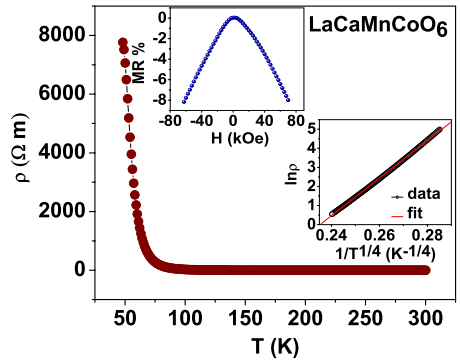

FIG. 3. (Color online) Temperature dependence of electrical resistivity of $LaCaMnCoO_6$. Insets show the $\ln\rho$ vs $1/T^{1/4}$ and MR% plots for the same compound.

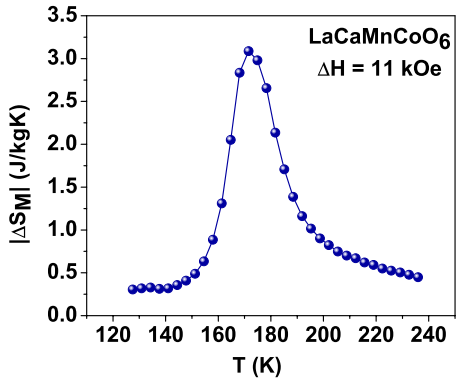

FIG. 4. (Color online) Temperature dependence of magnetic entropy change ($|\Delta S_M|$) in $LaCaMnCoO_6$ for a field change of 11 kOe.

pound has a semiconducting-like behavior and exhibits VRH-type conductivity above ~150 K. A maximum negative magnetoresistance of about 8% is obtained at 200 K in 7 T field. MCE is calculated from the magnetization data and maximum magnetic entropy change of ~3.1 J/kg K is observed near T_C for a field change of 11 kOe.

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