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Magnetic, magnetocaloric and critical behavior study of $La_{0.78}Pb_{0.22}MnO_3$ manganite near room-temperature

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ABSTRACT

We report the magnetic, magnetocaloric properties and critical behavior near transition temperature in $La_{0.78}Pb_{0.22}MnO_3$ perovskite manganite, prepared by solid state reaction method. Temperature dependence of magnetization exhibits a ferromagnetic to paramagnetic transition (T_C) at 292 K. Close to this transition, a maximum magnetic entropy change ($-\Delta S_M^{max}$) of 4.31 J/kg K and a relative cooling power (RCP) of 238 J/K are determined at a field of 5 T. Experimental results revealed that this sample underwent a second-order phase transition. Using the modified Arrott plot, Kouvel-Fisher method and critical isotherm analysis, the critical parameters (T_C, β, γ, and δ) have been determined. The estimated critical exponents (β=0.246, γ=0.929 and δ=4.49 at T_C=290.01 K) are found to be close to the tricritical mean-field model. These critical exponents fulfill the Widom scaling relation $\delta = 1 + \gamma/\beta$, implying the reliability of our values. On the basis of the obtained critical exponents, the magnetization-field -temperature (M-μ_0H-T) data around T_C are found to collapse into two curves by obeying the single scaling equation $M(\mu_0 H, \varepsilon) = (\varepsilon)^{\beta} f_{\pm}(\mu_0 H/\varepsilon^{\beta+\gamma})$ where $\varepsilon = T - T_C/T_C$, f_+ above and f_- below T_C, and confirm that the obtained values of β, γ and δ are reasonably accurate and unambiguous.

1. Introduction

Perovskite manganite materials with the general formula $RE_{1-x}AE_xMnO_3$ (RE=rare earth element and AE=bivalent alkaline metal) demonstrate some exciting properties such as the colossal magnetoresistance (CMR), multiferroic effects and charge and orbital ordering phenomena due to their strongly competing charge, spin and orbital ordering interactions [1–3]. Research in manganite materials has been flourished since the finding of higher magnetic entropy change on these materials that provide potential application in magnetic refrigeration [3,4]. Such refrigeration is based on magneto-caloric effect (MCE) and viewed as environmentally friendly and energy efficient in solid state cooling technology compared with conventional vapor compression approach. Hence, intensive research has been carried out to find desirable manganite material with higher magnetic entropy change and relative cooling power to work at room temperatures [4,5]. These materials have some advantages such as low production cost, good chemical stability, easy preparation and the ability to tailor their magnetic transition temperatures close to room temperature by varying the dopant and doping concentration [4]. These advantages indicate that the manganites can be appropriate for MCE when compared to the Gd-based metals and Heusler alloys.

Particularly, manganites doped with the divalent alkaline earth element $La_{1-x}A_xMnO_3$ (A=Sr, Ca, Ba, Pb, etc.,) have been investigated extensively for their enhanced ferromagnetism and metallicity [6,7]. Chau et al. [8] has studied the magnetic phase transition and MCE on $La_{1-x}Pb_xMnO_3$ compounds, and concluded that with a magnetic field varying from 0 to 13.5 kOe, the magnetic entropy change ($-\Delta S_M^{max}$) reaches a maximum value of about 0.65, 1.30, 1.53, 0.87, 0.81 J/kg K for x=0.1, 0.2, 0.3, 0.4, and 0.5, respectively. These reports suggest that the MCE can be enhanced with strong magneto-structural coupling and thereby it is worthwhile to investigate the nature of magnetic phase transition. Recent studies reported that, the investigation of critical behavior near the ferromagnetic-paramagnetic transition is a powerful tool to clarify the detailed magnetic interaction that responsible for the phase transition [9–11]. The common methods used to analyze and determine the theoretical critical values (β, γ and δ) are modified Arrott plot (MAP) [12], Kouvel-Fisher (KF) method [13], scaling-equation-of-

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state analysis [14] and the critical magnetization isotherm (CI). For instance, Tozri et. al., studied the $La_{0.8}Pb_{0.2}MnO_3$ sample and they obtained critical exponents of β=0.368, γ=1.324 and δ=4.77 whose values are between Mean-field model and 3D-Ising model [15].

The focus of the present paper is to study the magnetic, magneto-caloric effect and especially the critical behavior near the ferromagnetic (FM)–paramagnetic (PM) phase transition on $La_{0.78}Pb_{0.22}MnO_3$ (LPMO) compound. From the magnetic measurements, the sample shows a large magnetic entropy change of 4.31 J/kg K upon an applied field of 5 T at near room temperature (292 K). The relative cooling power (RCP) reaches as high as 238 J/K for a field of 5 T. The analysis of Arrott plot, landau theory and universal curve indicate that the ferromagnetic phase transition is of second order in LPMO. Further, to investigate the nature of the magnetic phase transition, a detailed critical exponent study around T_C has been performed using the techniques such as the Kouvel-Fisher method, the modified Arrott plot and critical isotherm analysis.

2. Experimental techniques

A conventional solid state reaction method is employed to prepare $La_{0.78}Pb_{0.22}MnO_3$ (LPMO) sample. In a standard procedure, stoichiometric mixtures of La_2O_3, PbO and MnO_2 (Sigma-Aldrich 99.9%) were taken according to the reaction:

$$0.39La_2O_3 + 0.22PbO + MnO_2 \rightarrow La_{0.78}Pb_{0.22}MnO_3 + \delta O_2 + \delta' CO_2$$

The starting materials was mixed in stoichiometric proportions, ground and then calcined at 900 °C for 48 h. Consecutively, the powder was pressed into pellet forms (of about 1 mm in thickness) under 4 tonnes/cm^2 and sintered in air at 1200 °C for 30 h with several periods of grinding and repelleting. Finally, those pellets were quenched at room temperature. This step was carried out so as to keep the structure at an annealing temperature.

The powder X-ray diffraction (XRD) was performed by the Bruker D8 X-ray diffractometer using Cu Kα radiation (1.5406 Å) at room temperature. The data collection was performed by step-scan modes, in a 2θ range between 19° and 99° and step time of 18 s. The diffraction pattern was analyzed with the use of the FullProf program that is based on the full-profile Rietveld method [16,17]. The magnetic measurements were carried out in a Superconducting Quantum Interference Device (**SQUID**) magnetometer. Magnetization of the samples was measured in an isothermal regime under an applied magnetic field varying from 0.5 to 5 T. In the vicinity of T_C (Curie temperature); isothermal M vs. H curves were obtained by a step of 3 K interval.

3. Results and discussions

3.1. Structural properties

Fig. 1 shows XRD patterns of the sample LPMO recorded at room temperature. From Fig. 1, we can note that the XRD profile exhibits a good agreement between observed and calculated profiles due to the excellent goodness of χ^2. There is no trace of any other secondary or impurity phase were detected. The sample is a single phase with rhombohedral structure ($R\bar{3}c$) in which La/Pb atoms are at 6a (0, 0, 1/4) position, Mn at 6b (0, 0, 0) and O at 18e (0.44, 0, 1/4) position. The estimated lattice parameters are a=b=5.5482 (5) A°; c=13.4108 (15) A°; α=β=90° and γ=120°. The refinement results are summarized in the Table 1.

3.2. Magnetic properties

Fig. 2 presents the temperature dependent magnetization, M(T), curve for LPMO sample in an applied field of 0.05 T. It is evident from the measurement that the sample undergo apparently ferromagnetic (FM)–paramagnetic (PM) phase transition at the Curie temperature

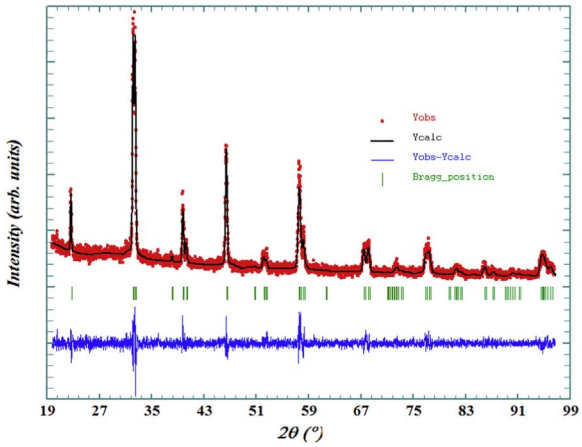

Fig. 1. Rietveld refinement for the sample $La_{0.78}Pb_{0.22}MnO_3$. Experimental data (the point symbols), calculated data (the solid lines), difference between them is shown at the bottom of the diagram and Bragg positions are marked by vertical bars.

Table 1
Results of Rietveld refinements, determined from XRD patterns measured at room temperature for LPMO sample.

Parameters	$La_{0.78}Pb_{0.22}MnO_3$
Structure type	Rhombohedral
Space group	$R\bar{3}c$
Lattice parameter	
a (Å)	5.548(5)
b (Å)	5.548(5)
c (Å)	13.410(15)
$V_{unit\ cell}$ (Å)	357.52
Mn-O(Å)	1.978(9)
Mn-O-Mn(°)	161.92(7)
Discrepancy factors(%)	
Bragg R-factor	7.478
R_p	47.4
R_{wp}	33.4
R_{exp}	29.53
RF-factor	6.292
Goodness of fit χ^2	1.28

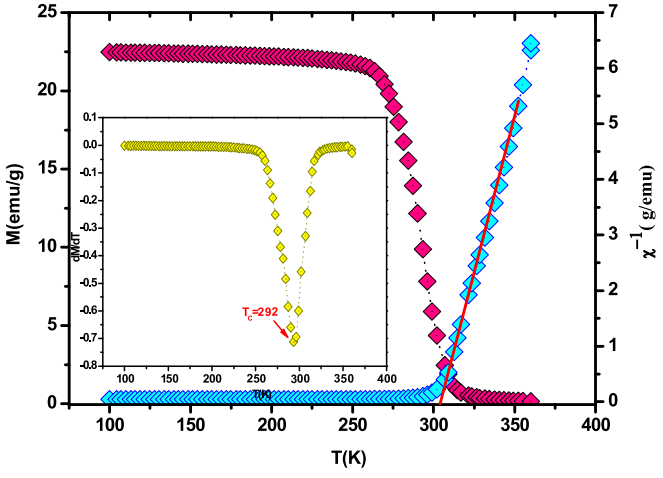

Fig. 2. Temperature dependence of magnetization M(T) measured at 0.05 T and the inverse magnetic susceptibility curve measured at 0.05 T as a function of temperature for: LPMO (the solid line is the linear fit to the susceptibility data according to Curie–Weiss law above T_C). The inset shows the plot of dM/dT as a function of temperature at $\mu_0 H$=0.05 T.