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Magnetic and magnetocaloric properties in second-order phase transition $La_{1-x}K_xMnO_3$ and their composites

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ABSTRACT

In this work, we present a detailed study on the magnetic properties and the magnetocaloric effect (MCE) of $La_{1-x}K_xMnO_3$ compounds with x=0.05–0.2. Our results pointed out that the Curie temperature (T_C) could be controlled easily from 213 to 306 K by increasing K-doping concentration (x) from 0.05 to 0.2. In the paramagnetic region, the inverse of the susceptibility can be analyzed by using the Curie-Weiss law, $\chi(T)=C/(T-\theta)$. The results have proved an existence of ferromagnetic clusters at temperatures above T_C. Based on Banerjee's criteria, we also pointed out that the samples are the second-order phase transition materials. Their magnetic entropy change was calculated by using the Maxwell relation and a phenomenological model. Interestingly, the samples with x=0.1–0.2 exhibit a large MCE in a range of 282–306 K, which are suitable for room-temperature magnetic refrigeration applications. The composites obtained from single phase samples (x=0.1–0.2) exhibit the high relative cooling power values in a wide temperature range. From the viewpoint of the refrigerant capacity, the composites formed out of $La_{1-x}K_xMnO_3$ will become more useful for magnetic refrigeration applications around room-temperature.

1. Introduction

The magnetocaloric effect (MCE) is warming or cooling of a magnetic material in response to the application or removal of an external magnetic field, which was discovered in 1881 by Warburg [1]. Their magnitude is characterized by the isothermal magnetic entropy change (ΔS_m) or by the adiabatic temperature change (ΔT_{ad}) due to an applied magnetic field change. The magnetic refrigeration based on the MCE becomes a new technique that is more efficient and environmentally friendly [2]. The previous reports showed that Gd metal with T_C=294 K exhibits a high MCE corresponding to a large value of the relative cooling power (RCP=63.4 J/kg at 10 kOe) [3]. Gd metal can be thus used as a prototype magnetic material for applications in the room-temperature magnetic refrigeration [3,4]. Unfortunately, Gd is very expensive. Thus, in the last two decades, the scientists have spent much time and effort to find new cheap materials, which have the large MCEs at around room-temperature. Among these, perovskite manganites with a general formula $LnMnO_3$ (*Ln* is a rare-earth element) are also believed to be good candidate for applicability in magnetic cooling technology.

Concerning perovskite manganites, which have been investigated since 1950s due to richness in their structural and the electrical-magnetic properties [5]. It is known that $LnMnO_3$ is an anti-ferromagnetic (anti-FM) insulator, but substituting the *Ln*-site by an alkali earth or alkali element (*M*) to formulate $Ln_{1-x}M_xMnO_3$ leads to the conversion of $Mn^{3+}(t_{2g}^3e_g^1, S=2)$ ions into $Mn^{4+}(t_{2g}^3, S=3/2)$ ions, and creates the mobile e_g electrons. The ferromagnetic (FM) double-exchange interaction of the Mn^{3+}-Mn^{4+} ions pair will appear. Then, the material exhibits a FM-paramagnetic (PM) phase transition at the Curie temperature (T_C), and some unusual physical properties, such as the colossal magnetoresistance and the MCE. The electrical-magnetic properties of $Ln_{1-x}M_xMnO_3$ are strongly affected by the structure parameters, such as Mn-O bond length, Mn-O-Mn bond angle, and Goldsmith tolerance factor (t). However, these parameters can be controlled by the changes of average ionic radii at *Ln*/*M* site, Mn site, and/or Mn^{3+}/Mn^{4+} ratio, which modify the strength and the order of the FM interactions in manganites [6]. The influences of alkali elements (*M*=Na, Ag, K...) doped into *Ln*-site on the magnetic and

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transport properties, as well as MCE of La-based perovskite manganites (*Ln*=La) have been regarded in some previous studies [7–9]. However, the detailed investigations on the MCE properties of $La_{1-x}K_xMnO_3$ compounds as well as their composites are still lacking and therefore this content needs a deep more assessment.

In this work, the influence of K-doping on the magnetic and magnetocaloric properties of $La_{1-x}K_xMnO_3$ compounds has been investigated. Their MCE has been calculated via both the experimental data and the theoretical approaching method. Our results have also revealed that the composites, which are combined from two or three single phase samples (with x=0.1–0.2) exhibit the large MCE in a wide temperature range about 33–50 K, making $La_{1-x}K_xMnO_3$ more useful for magnetic cooling applications.

2. Experimental

Four polycrystalline samples of $La_{1-x}K_xMnO_3$ with x=0.05, 0.1, 0.15, and 0.2 were prepared by a solid-state reaction technique. The precursors are La_2O_3, $KMnO_4$, and MnO powders that were ground and mixed well in the stoichiometric ratios and then calcinated in air at 700 °C for 12 h. The obtained mixtures were re-ground and mixed, and pressed into pellets under a pressure 5000 psi, and then sintered at 1100 °C for 12 h in air. Finally, these pellets were sintered at 1200 °C for 12 h in air. Four bulk composites (denoted as C1, C2, C3, and C4) were formed from two or three single phase samples prepared above with x=0.1, 0.15 and 0.2 in the powder form. The mass of composites was calculated as following

$$m_{C1} = ½\, m_{(x=0.1)} + ½\, m_{(x=0.15)} \quad (1)$$

$$m_{C2} = 1/2\, m_{(x=0.15)} + 1/2\, m_{(x=0.2)} \quad (2)$$

$$m_{C3} = 1/2\, m_{(x=0.1)} + 1/2\, m_{(x=0.2)} \quad (3)$$

$$m_{C4} = 1/3\, m_{(x=0.1)} + 1/3\, m_{(x=0.15)} + 1/3\, m_{(x=0.2)} \quad (4)$$

where, $m_{(x=0.1)}$, $m_{(x=0.15)}$, and $m_{(x=0.2)}$ are the mass of samples x=0.1, 0.15, and 0.2, respectively. These powders combined with the same mass were mixed and pressed into pellets under a pressure 5000 psi, and then calcinated at 700 °C for 5 h in air. The phase purity of the samples was checked by an X-ray diffractometer (Bruker AXS, D8 Discover) using a Cu-K_α radiation source at room-temperature. The magnetic properties versus temperature (in the range of 100–350 K) and the magnetic field (up to 10 kOe) were performed on a vibrating sample magnetometer (VSM), herein the $M(H)$ curves were measured around T_C for each sample with a temperature interval of 2 K.

3. Results and discussions

X-ray diffraction (XRD) patterns at room-temperature of $La_{1-x}K_xMnO_3$ samples with x=0.05–0.2 are presented in Fig. 1(a). It indicates that all the samples are single phase of $La_{1-x}K_xMnO_3$, without any trace of secondary phase. All XRD peaks are sharp and narrow indicating the samples are high crystallized and homogeneous. The Miller-indexes of all XRD peaks belong to a hexagonal structure, space group *R*3-*c*. Fig. 1(b) shows XRD patterns of four composites C1-C4, which are similar with those obtained for separate samples, and their XRD patterns also belong to a hexagonal structure. It is not easy to observe the difference between the XRD patterns of separate samples with composites because the XRD patterns of separate samples are very close to each other, therefore, these patterns are overlapped in composites. Non-unusual XRD peak was observed, suggesting that there is no intermediate phase and no chemical reaction took place when these composites were calcinated at 700 °C for 5 h in air. It means that this calcination simply makes separate phases mechanically bonded to each other.

The temperature dependence of the normalized magnetization $M(T)/M(100\ K)$ measured at 100 Oe for $La_{1-x}K_xMnO_3$ samples with x=0.05, 0.1, 0.15, and 0.2 are presented in Fig. 2(a). All the samples exhibit a magnetic phase transition from FM state to PM state, which is associated with $La_{1-x}K_xMnO_3$ manganite phase in the samples [8,9]. This FM-PM phase transition is effectively tuned to higher temperature by increasing potassium content. T_C value of the samples was determined at the minimum position of the dM/dT versus T curves, the inset in Fig. 2(a). T_C values are thus found to be 213, 282, 296, and 306 K for x=0.05, 0.1, 0.15, and 0.2, respectively. There is a difference with those reported that T_C=271 K for x=0.1 and 324 K for x=0.15 in Refs. [8,9], which could be related to the difference in sample-preparation conditions (for example, the sample-preparation method, sintered temperature and time). However, their variation tendency of T_C with increasing K-content is the same.

Fig. 2(b) shows the temperature dependence of the inverse magnetic susceptibility $\chi^{-1}(T)$ for samples. Clearly, above T_C, $\chi^{-1}(T)$ curves exhibit the linear behavior, which can be fitted to the Curie-Weiss law, $\chi(T)=C/(T-\theta)$ [10], where C is the Curie constant and θ is the Curie-Weiss temperature. The θ values of samples are listed in Table 1. Herein, the T_C and θ values increase with increasing K concentration, see the inset in Fig. 2(b), suggesting the strength of the FM interactions is enhanced in high-doping level samples. This could be related to an increase in the average ionic radius of *A*-site in ABO_3 structure that is defined as $<r_A> = (1-x)r_{La3+} + (x)r_{K+}$ (see Table 1), [11], which is consistent with the fact that the ionic radius of K^+ is larger than that of La^{3+} (r_{K+} =1.64 Å and r_{La3+}=1.36 Å, based on the appropriate XII coordinate radii of Shannon [12]). Besides, for each sample, θ value is higher than T_C, which could be related to an existence of FM clusters in the PM region. Based on the Curie constant C obtained from fitting above, the experimental effective paramagnetic moment (μ_{eff}^{exp}) of $La_{1-x}K_xMnO_3$ was determined following the relation $C=N_A(\mu_B\mu_{eff}^{exp})^2/3k_B$, where N_A=6.023×10^{23} mol^{-1}, k_B=1.3806×10^{-23} J/K. The values of μ_{eff}^{exp} for samples are given in Table 1. However, in the PM region, there are only the contribution of free magnetic moments of Mn^{3+} and Mn^{4+} ions to the PM susceptibility of $La_{1-x}K_xMnO_3$ compounds. Thus their effective paramagnetic moment μ_{eff}^{theo} could be calculated as followed: $(\mu_{eff}^{theo})^2=(1-2x)(\mu_{eff}^{Mn3+})^2+2x(\mu_{eff}^{Mn4+})^2$ with μ_{eff}^{Mn3+}=4.90 μ_B and μ_{eff}^{Mn4+}=3.87 μ_B [13]. The values of μ_{eff}^{theo} calculated for $La_{1-x}K_xMnO_3$ compounds are listed in Table 1. Clearly, μ_{eff}^{theo} values are smaller than μ_{eff}^{exp}, suggesting an existence of FM clusters due to the double exchange interaction of Mn^{3+}-Mn^{4+} pairs in the PM region [14].

Fig. 3 shows $M(H)$ curves measured at various temperatures around the FM-PM phase transition under the applied field up to 10 kOe for two representative samples with x=0.05 and 0.2. We can see that the magnetization of samples increases most abruptly in low-field range and then approaches to saturation of above 2 kOe. The nonlinear $M(H)$ curves become linear when the magnetic property of sample transfers from the FM to the PM state. There is a drive towards two opposite directions of H/M versus M^2 curves at temperatures below and above T_C (the insets of Fig. 3), which is related to the FM-PM phase separation behavior in the samples. Clearly, the slope of H/M versus M^2 curves is positive proving that the samples are second-order phase transition (SOPT) materials [15].

For a magnetic material, the change in the magnetic entropy can be deduced from the Maxwell relation [10]

$$\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial M}{\partial T}\right)_H, \quad (5)$$

Integrating Eq. (5), we obtain the isothermal magnetic entropy change under an applied magnetic field change from 0 to H as below

$$\Delta S_m = S(H,T) - S(0,T) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH, \quad (6)$$

where H is the applied field magnitude.

Recently, a new phenomenological model has been proposed

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