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Phase separation and magnetocaloric effect in $Pr_{0.5-x}Gd_x$ $Sr_{0.5}MnO_3$ system

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ABSTRACT

The magnetic properties and the magnetocaloric effect have been studied in $Pr_{0.5-x}Gd_xSr_{0.5}MnO_3$ (x = 0, 0.05 and 0.1) manganites prepared by the solid state reaction method. Magnetic measurements versus temperature in an applied magnetic field of 0.05 T show that the all samples exhibit a paramagnetic to ferromagnetic transition when temperature decreases. The x = 0.1 sample shows a clear transition, from the ferromagnetic state to the antiferromagnetic one at T_N = 125 K. The Curie temperature decreases gradually with increasing gadolinium content. The absolute values of the maximum of magnetic entropy change $|\Delta S_M|$ for an applied magnetic field of 2 T are equal to1.26, 1.25 and 1.02 J kg^{-1} K^{-1} for x = 0, 0.05 and 0.1, respectively. The decrease of $|\Delta S_M|$ with Gd doping can be attributed to the enhancement of phase separation phenomenon. The magnetic entropy curves follow the universal law corresponding to the second-ordered paramagnetic-ferromagnetic transition.

1. Introduction

The perovskite manganites with general formula $T_{1-x}D_xMnO_3$ (T is a trivalent rare earth ion and D is a divalent alkaline-earth ion) have been intensively investigated in the last decades because of their potential applications in several fields. Magnetic and electrical transitions, colossal magnetoresistance (CMR) as well as magnetocaloric effect (MCE) [1–7] gave renewed interest in perovskite manganites. Double-exchange interactions between Mn^{3+} and Mn^{4+} ions were used in order to interpret the CMR effect. The MCE is an intrinsic property of magnetic materials; it originates from their heating due to the adiabatic application of magnetic field. The gadolinium is known as the best candidate for magnetic refrigeration because of its large magnetic entropy change ΔS_M which is about 10.2 J kg^{-1} K^{-1} for a magnetic field change of 5 T [8].

Half doped perovskite manganites with x value equal to 0.5 possess equal amounts of Mn^{3+} and Mn^{4+} ions [1,3,9–14]. The half doped compounds are generally characterized by a very important CMR effect compared to MCE. These compounds are also characterized by the complexity of the electrical and magnetic behavior as well as phase separation phenomenon consisting in the coexistence of two or more different magnetic phases. $Pr_{0.5}Sr_{0.5}MnO_3$, with an average ionic radius at A-site $\langle r_A \rangle$ of 1.245 Å, is one of the most studied compounds in the last years [1,15–21]. This compound received much attention due to the discovery of the first ordered antiferromagnetic insulator-ferromagnetic metal transition under a magnetic field recorded at Néel temperature T_N. This compound presents a magnetic transition from the paramagnetic (PM) state to the ferromagnetic (FM) state at T_C = 260 K, this transition is followed by another one to the antiferromagnetic (AFM) state at T_N = 150 K. It is also characterized by the phase separation phenomenon, with the appearance of AFM clusters just below the Curie temperature [20].

Gadolinium ions Gd^{3+} possess an important magnetic moment and a small ionic radius compared to praseodymium ions Pr^{3+}. The substitution of Pr ions by Gd ones will certainly affect the ordering inside the structure. Such doping will enhance both structural and magnetic disorder. Thus, the $Pr_{0.5-x}Gd_xSr_{0.5}MnO_3$ system seems to be very important in order to study the effect of disorder on phase separation without changing the amount of Mn^{3+} and Mn^{4+} ions. The electrical properties of $Pr_{0.5-x}Gd_xSr_{0.5}MnO_3$ (x = 0, 0.05 and 0.1) samples have been previously reported [21]. The magneto-transport study has shown that our samples exhibit different electrical behavior as a function of temperature. The Gd doping increases the resistivity and magnetoresistance values especially at low temperature values [21]. In this work, we are interested to investigate the magnetic properties of these samples.

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2. Experimental details

A series of polycrystalline $Pr_{0.5-x}Gd_xSr_{0.5}MnO_3$ samples were prepared by the conventional solid state reaction method. High purity Pr_6O_{11}, Gd_2O_3, $SrCO_3$ and MnO_2 up to 99.9% were mixed in stoichiometric proportions. The mixture was first heated at 1000 °C for 24 h. After that, all the samples were repeatedly ground and heated for 20 h at 1000 °C. Then, the powders were pressed into pellets of about 2 mm of thickness and sintered at 1200 °C in air for 60 h with intermediate regrinding and repelling. This procedure is necessary to ensure complete reaction and a homogeneous distribution of cations. We should note that the substitution of Gd^{3+} for Pr^{3+} would not influence the ratio Mn^{3+}/Mn^{4+} since $Pr^{3+}$and Gd^{3+} have the same valence. The single phase nature and phase purity was confirmed by X-ray powder diffraction. The magnetization measurements versus temperature and versus magnetic field were performed in the temperature range 4–340 K up to 7 T using a vibrating sample magnetometer.

3. Results and discussions

The $Pr_{0.5-x}Gd_xSr_{0.5}MnO_3$ samples were indexed in orthorhombic system with *Pbnm* space group. The increase of Gd content leads to the decrease of the average ionic radius of the A site $\langle r_A \rangle$ as well as an increase of the mismatch effect σ^2 [21]. Fig. 1 shows the temperature dependence of the field cooled (FC) and the zero field cooled (ZFC) magnetization M (T) for all our specimens in the temperature range 4–330 K with an applied magnetic field of 0.05 T. All samples present a transition from PM to FM state at T_C when the temperature decreases. The value of T_C, defined as the temperature of the maximum slope in dM/dT, decreases with increasing gadolinium content. The decrease of T_C values can be explained by the cooperative contribution of $\langle r_A \rangle$ and σ^2. In fact, the introduction of Gd into Pr-site leads to the increase of the cationic disorder of A site σ^2 and the reduction of the average ion radius of the A cation site $\langle r_A \rangle$. This will certainly increase the contribution of super exchange mechanism in favor of double exchange one. This will yield a decrease of FM tendencies and can explain the decrease of T_C. Similar results were obtained for some Gd-based manganites [22–25].

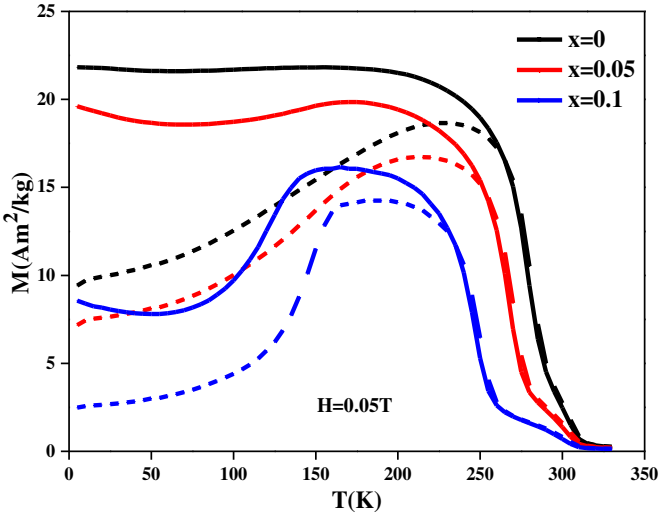

Fig. 1. Temperature dependence of FC (solid line) and ZFC (dashed line) magnetization for the $Pr_{0.5-x}Gd_xSr_{0.5}MnO_3$ (x = 0, 0.05 and 0.1) samples under magnetic applied field of 0.05 T.

At low temperatures, all our compounds indicate an AFM behavior which is obviously detected from ZFC curves. The x = 0.1 sample shows two distinct transitions, one from PM to FM state at T_C = 250 K, this transition is followed by another one to AFM state at T_N = 125 K. It is seen that the FM-AFM transition is not clear for x = 0 and x = 0.05 samples in the FC magnetization curve. We can note that the gadolinium doping reinforces the AFM state. This is confirmed by the electrical properties when all the samples present an insulating behavior and explains the improvement of the magnetoresistance at low temperatures [21]. This system is also characterized by the phase separation phenomenon. Such phenomenon was confirmed by the large difference between M_{FC} and M_{ZFC} below the Curie temperature. This difference is found to decrease with an increase in the Gd content, which confirms the enhancement of AFM.

In order to clarify the magnetic behavior of our studied samples, the evolution of magnetization as a function of the applied magnetic field was shown in Fig. 2. The isothermal magnetization data shows that the magnetization strongly increases with increasing applied field for $\mu_0 H \leq 1$ T which confirms that the ground state of our samples is FM. For the compounds with x = 0 and x = 0.05, we can see for low magnetic field values (0 T < μ_0H < 1 T), an overlapping of magnetization curves which can be attributed to the existence of some AFM clusters. For the sample with x = 0.1, the presence of the AFM state is evident through the metamagnetic transition observed in isothermal curves for temperature values lower than 160 K. Above this temperature value, this sample behaves like a traditional ferromagnetic specimen. Thus, one can say that all our studied samples are characterized by phase separation phenomenon. Besides, it is clear that Gd doping enhances the fraction of the AFM clusters which indicates an enhancement of super exchange interactions in favor of double exchange ones. The magnetic results for our samples agree with the electrical study [21].

We can also notice that M (H) curves are not linear for our samples just above T_C which can be explained by the presence of some ferromagnetic clusters in the paramagnetic phase [26]. The saturation magnetization recorded at 4 K for a magnetic applied field of 7 T is about 2.94, 3.27 and 2.19 μ_B/Mn, for the x = 0, 0.05 and 0.1 samples, respectively. All these values are lower than theoretical moment obtained by full spin alignment (3.5 μ_B/Mn) which supposes the persistence of AFM clusters. Normally, saturation magnetization should decrease due to the enhancement of AFM tendencies. However, it seems that the x = 0.05 sample has something special which enhances the volume fraction of FM domains in favor of AFM ones. This can be attributed to the disorder induced by 5% Gd at the A-site. But, with further increase of Gd content, more AFM ordering is established inside the structure.

Fig. 3 shows the standard Arrott plots (the square of the magnetization M^2 according to $\mu_0 H/M$ for each temperature) for all our samples. All the curves for all the samples present positive slopes near T_C, which indicates that these samples present a second ordered transition from FM to PM state. If we check M (T) curves (Fig. 1) we can notice that the FM-PM transition is large (broad transition) which supports the idea that the transition is of second order. Such observation can be explained by the phase separation phenomenon due to the simultaneous coexistence of FM and AFM domains just below T_C [20]. For the compound with x = 0.1, the presence of isotherms with negative slopes around T_N confirms the first-ordered nature of this transition.

In the PM region, the temperature dependence of the inverse of the PM susceptibility is shown in Fig. 4. The temperature dependence of the inverse of susceptibility χ^{-1} for high temperatures is given by the following formula: