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Bi doping effect on the critical behavior and magnetocaloric effect of $Pr_{0.8-x}Bi_xSr_{0.2}$ MnO_3 (x = 0, 0.05 and 0.1)

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ABSTRACT

In this study, we report the effect of Bi doping on the critical behavior and the magnetocaloric properties of $Pr_{0.8-x}Bi_xSr_{0.2}MnO_3$ (x = 0, 0.05 and 0.1) structures prepared by sol-gel method. Refined values of the critical exponents β, γ, and δ determined from the modified Arrott plots and Kouvel–Fisher method show that the parent sample is described by the tricritical mean field model whereas the 3D-Ising model is the best model describing doped samples. Consequently, a transition from long-range to short range FM interactions caused by the introduction of Bi in the parent sample can be identified. All samples reveal the presence of some ferromagnetic domains in the paramagnetic phase. In the vicinity of the Curie temperature T_C and for an applied magnetic field of 5 T, the maximum of magnetic entropy change $|\Delta S_M|$ decreases from 5.41 J $K^{-1}kg^{-1}$ for x = 0–3.11 J $K^{-1}kg^{-1}$ for x = 0.1, respectively. The $|\Delta S_M|$ for doped samples exhibits a large broad variation with temperature around T_C as compared with the parent sample. Such effect is substantially advantageous for magnetic refrigeration. Also, the magnetocaloric effect is investigated using Landau theory. A good agreement is obtained between this theory and experimental data, which suggests that electronic interactions and magnetoelastic coupling are at the origin of the magnetocaloric properties of our samples. In addition, we report that $|\Delta S_M|$ curves follow the universal law confirming the second-ordered paramagnetic-ferromagnetic transition.

1. Introduction

Perovskite-type manganite oxides with the general formula $T_{1-x}D_xMnO_3$ where T is a trivalent rare earth (Pr, La, Nd, …) and D a divalent (Sr, Ca, Ba …) or monovalent alkaline earth (Ag, K, Na, …), are intensively studied in the last decades owing to their rich physical properties. These materials can be potential candidates for large applications such as magnetic recording devices, magnetic sensors, infrared detectors, thermoelectric applications and non-polluting magnetic refrigerants [1–4]. The discovery of colossal magnetoresistance and the important magnetocaloric properties [5,6] open up new horizons for other exciting innovations. Nevertheless, the most interesting challenge now is to select among these manganites the smartest one with a broad magnetocaloric effect (MCE) not only near the room temperature but also at lower temperatures thanks to the possibility of to their use in several applications such as gas liquefaction and natural gas [7].

A giant MCE is discovered in structures such as $Gd_5(Si_2Ge_2)$ and $LaFe_{11.4}Si_{1.6}$ [8,9]. The $MnFeP_{0.45}As_{0.55}$ system allows magnetic refrigeration at room temperature thanks to its magnetic entropy change evaluated at 14.5 J K^{-1} kg^{-1} and 18 J K^{-1} kg^{-1} for field changes of 2 T and 5 T, respectively [10]. Another interesting structure is the MnAs which shows a magnetic entropy change estimated at 30 J K^{-1}kg-1 under an applied magnetic field of 5 T. This value exceeds that of most conventional magnetic refrigerant materials by a factor of 2–4 owing to the first-ordered ferromagnetic to paramagnetic transition [11].

At low temperatures, binary R-T (where R = Pr, Gd, Tb, Dy, Ho, Er, Tm and T = Ga, Ni, Co, Cu) intermetallic compounds (including RGa, RNi, $R_{12}Co_7$, R_3Co and RCu_2 series) exhibit excellent MCE which makes them in the basis of potential applications such as gas liquefaction [12].

On other hand, the $Er_{12}Co_7$ compound show high magnetic entropy change values which reach 10.2 J K^{-1} kg^{-1} and 18.3 J K^{-1} kg^{-1} under an applied magnetic field changes of 0–2 T and 0–5 T respectively [13]. In the $Ho_{0.1}Er_{0.9}Ni$ compound, the magnetic entropy change is 34 J K^{-1} kg^{-1} under a magnetic field change of 0–5 T [14]. Zheng et al. [15] have demonstrated that

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among RCu_2 (R = Tb, Dy, Ho and Er) compounds, $TbCu_2$ and $DyCu_2$ show large inverse MCE under a field change of 0–7 T around the transition temperature. Structures such as $La_{1-x}K_xMnO_3$ ($x = 0.11$, 0.13, 0.15) [16] and $(La_{1-x}Pr_x)_{0.67}Pb_{0.33}MnO_3$ ($0.0 \leq x \leq 0.3$) [17] have been also explored. In addition, $Pr_{1-x}Sr_xMnO_3$ compounds exhibit very interesting properties due to their rich phase diagram [18]. Praseodymium substitution by Bismuth, induces in these structures a decrease in the Curie temperature which is explained by the presence of the highly polarizable $6s^2$ lone pair electrons of Bi^{3+} and leads to the decrease of overlapping between the 3d orbital of the Mn ions and the 2p orbital of the oxygen anion [19,20]. Most studies in literature were interested in the effect of Bi-doping on physical properties of La-based manganites [21]. There is no previous works, as we know, which investigate Bi-doping in the $Pr_{0.8}Sr_{0.2}MnO_3$ compound. In our laboratory, Elghoul et al. and Kammoun et al. have studied the effect of Bi-doping in $Pr_{0.63}Bi_{0.07}Sr_{0.3}MnO_3$ (in A-site) and in $Pr_{0.6}Sr_{0.4}Mn_{1-x}Bi_xO_3$ (in B-site) and have obtained interesting results [22,23]. Doping praseodymium-based compounds by bismuth further improves their magnetic response and leads to the appearance of high magnetocaloric effect [22]. To understand the nature of the FM–PM transition near the critical transition temperature T_C, it is necessary to study the critical behavior by analysing the critical exponents β, γ, and δ. Four models were proposed depending on the range of magnetic interactions: The mean-field model, the tricritical mean field model, the Heisenberg model and the 3D-Ising model. In literature, several values were reported for the critical parameters of perovskite manganites. These values were a subject of a controversy since they belong to different models covering the range between long and short range interactions [24–26]. We are interested in the $Pr_{0.8}Sr_{0.2}MnO_3$ structure. Magnetic properties of this compound have been studied [27,28] but to our knowledge, no studies on the critical behavior of such system have been reported.

In this work, we report the critical behavior near the Curie temperature T_C and the magnetocaloric properties of $Pr_{0.8-x}Bi_xSr_{0.2}MnO_3$ (PBSMO) compounds with x = 0; 0.05 and 0.1.

The critical behavior of our samples is studied using the modified Arrott-Noakes plots (MAP), the Kouvel-Fisher (KF) as well as the critical isotherm (CI) method. Then, the critical exponents of each compound are calculated in order to determine the nature of the magnetic interactions. In addition, attention is paid to the Bi doping effect on the magnetic entropy change ΔS_M.

2. Experimental details

$Pr_{0.8-x}Bi_xSr_{0.2}MnO_3$ (x = 0, 0.05 and 0.1) polycrystalline samples were synthesized using the sol-gel process by mixing high purity Pr_6O_{11}, Bi_2O_3, $SrCO_3$ and MnO_2 precursors (purities up to 99.9%) in the desired proportion as described in our previous work [29]. Homogeneity and phase purity of the studied samples were carried out by X-ray diffraction at room temperature using CuKα radiation (λ = 1,5406 Å). The structure refinement was carried out by Rietveld analysis. It was found that our samples are single phase and crystallize in the orthorhombic structure with *Pnma* group space [29].

For the magnetic measurements versus temperature M(T) and magnetic field M(μ_0H), a vibrating sample magnetometer (SQUID VSM, Quantum Design) was used in the temperature range 5–330 K and magnetic fields up to 5 T.

3. Results and discussion

3.1. Magnetic results

Fig. 1 displays the temperature dependence of normalized magnetization (M/M(T = 5 K) under an applied magnetic field of 0.05 T for $Pr_{0.8-x}Bi_xSr_{0.2}MnO_3$ (x = 0, 0.05 and 0.1) compounds. As shown, the obtained curves revealed that our samples undergo a paramagnetic (PM) to ferromagnetic (FM) transition with decreasing temperature. In the same figure, we have plotted in the two insets the evolution of d^2M/dT^2 and the inverse of magnetic susceptibility χ versus temperature in the paramagnetic region. The Curie-temperature for each compound is determined from the curve d^2M/dT^2 at $d^2M/dT^2 = 0$. The linear behavior of χ^{-1} versus temperature shows that χ follows the Curie-Weiss law $\chi = C_p/(T - \theta_p)$ where C_p is the Curie constant and θ_p, the Weiss temperature. The values of T_C and θ_p are listed in Table 1. As seen, the decrease of θ_p which is associated to the decrease of T_C, indicates the weakening of the double exchange mechanism in our structures [30]. In addition, the difference observed between T_C and θ_p values can be correlated with the persistence of a short-range magnetic ordering that occurs slightly above T_C. Such behavior can be explained by the existence of some magnetic inhomogeneities in the PM [31].

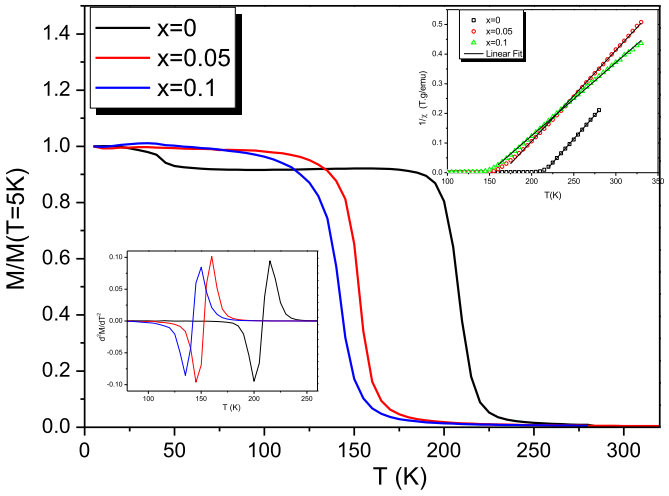

Fig. 1. Temperature dependence of the normalized magnetization M/M(T = 5 K) under a magnetic applied field of 0.05 T for $Pr_{0.8-x}Bi_xSr_{0.2}MnO_3$ (x = 0, 0.05 and 0.1) compounds. The insets show the temperature evolution of d^2M/dT^2 and χ^{-1} versus temperature.

3.2. Critical behavior

Using the experimental magnetization data obtained for all studied compounds, we have determined the modified Arrott-Noakes plots (MAP) in order to better focus on the nature of the transition around the Curie-temperature. These curves are obtained from the equation [32]:

$$\left(\frac{\mu_0 H}{M}\right)^{\frac{1}{\gamma}} = \frac{(T - T_C)}{T_C} + \left(\frac{M}{M_1}\right)^{\frac{1}{\beta}} \quad (1)$$

where M_1 represents a constant, γ and β the critical exponents. As known, β describes the spontaneous magnetization at low temperatures ($T < T_C$) and γ is related to the inverse of susceptibility determined at high temperatures ($T > T_C$).

Table 1
Curie temperature T_C and Curie-Weiss temperature θ_p of the $Pr_{0.8-x}Bi_xSr_{0.2}MnO_3$ (x = 0, 0.05 and 0.1) compounds.

Compound	x = 0	x = 0.05	x = 0.1
T_C (K)	210	155	140
θ_p (K)	214.246	165.408	133.692