



# Effect of monovalent metal substitution on the magnetocaloric effect of perovskite manganites $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{M}_{0.2}\text{MnO}_3$ ( $\text{M}=\text{Na}, \text{Li}, \text{K}$ and $\text{Ag}$ )

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## ABSTRACT

The influence of monovalent doping on the magnetocaloric effect (MCE) and refrigerant capacity or relative cooling power (RCP) of  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{M}_{0.2}\text{MnO}_3$  ( $\text{M}=\text{Na}, \text{Li}, \text{K}$  and  $\text{Ag}$ ) materials has been investigated. A large magnetocaloric effect was inferred over a wide range of temperature around the second order paramagnetic–ferromagnetic transition. The maximum magnetic entropy changes ( $\Delta S_M$ ) reached 1.8, 2.2, 1.6 and 2.1 J/kg K and the relative cooling power (RCP) approached 58.9, 59.3, 69.6 and 54.6 J/kg for Na, Li, K and Ag doped materials in the magnetic change of 15 kOe, respectively. According to the results determined by the Maxwell relation, the magnetic entropy change fits well with the Landau theory of phase transition above  $T_C$  for  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{Li}_{0.2}\text{MnO}_3$ . The large magnetic entropy change induced by low magnetic field suggested that these materials are beneficial for practical applications.

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## 1. Introduction

Magnetic refrigeration (MR), which is a technology used to warm and cool in response to application and removal of an external magnetic field, gets comprehensive attention due to its several apparent advantages over vapor compression refrigeration: high cooling efficiency, environmentally friendly technology and convenient for miniaturization [1]. MR is based on the magnetocaloric effect which is determined by the isothermal magnetic entropy change and adiabatic temperature change. To find an active magnetic refrigerant (AMR) working at room temperature, most researchers focus on the metal alloys. These refrigerants, e.g. Gd [2],  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  [3],  $\text{LaFeSi}$  [4], undergoing the first-order magnetic transition, generally have large magnetic entropy changes. It should be noticed that although the first-order transition is able to concentrate the MCE in a narrow temperature range and this produces large magnetic entropy changes, the RCP becomes small. Furthermore, material with a large MCE undergoing first order transition is always in a high magnetic field and has considerable hysteresis.

Refrigerants of manganites undergoing second-order magnetic transition with a large MCE take a resurgence of interest due to their low hysteresis, affluent metamagnetic transition and coupling between charge and lattice. The MCE of  $\text{Pr}_{1-x}\text{Sr}_x\text{MnO}_3$  ( $0.3 < x < 0.5$ ) polycrystalline manganites was reported by Chen

et al. [5], who found the maximum of  $\Delta S_M$  of 7.1 J/kg K at 161 K for 10 kOe for the  $x=0.5$  samples. However, the Curie temperature ( $T_C$ ) is far from room temperature, limiting their practical applications. Koubaa et al. [6], investigated the MCE properties of  $\text{La}_{0.8}\text{Ag}_{0.1}\text{Na}_{0.1}\text{MnO}_3$  and  $\text{La}_{0.8}\text{Ag}_{0.1}\text{K}_{0.1}\text{MnO}_3$  that reached 4.39 and 4.92 J/kg K and the Curie temperatures reached 320 K and 310 K for Na and Ag for 50 kOe magnetic field changes, respectively. Das and Dey [7,8], also did a lot of work on monovalent elements doped perovskite systems; it was found that the Curie temperature of  $\text{La}_{1-x}\text{K}_x\text{MnO}_3$  strongly depends on K content and the enhancement of magnetic entropy change was observed also. Thus, materials with monovalent elements doping at A-sites increase the Curie temperature without distinct decrease in the MCE.

In the present work, we investigate the effect of the same monovalent metal content of Na, Li, K and Ag substitution on the structural, the magnetocaloric properties and the Curie temperature of  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{M}_{0.2}\text{MnO}_3$  ( $\text{M}=\text{Na}, \text{Li}, \text{K}$  and  $\text{Ag}$ ).

## 2. Experimental details

Powder samples of  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{M}_{0.2}\text{MnO}_3$  ( $\text{M}=\text{Na}, \text{Li}, \text{K}$  and  $\text{Ag}$ ) have been synthesized by using the standard solid state reaction method at high temperature. The starting materials ( $\text{Pr}_6\text{O}_{11}$ ,  $\text{SrCO}_3$ ,  $\text{MnCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ) were mixed in an agate mortar. After ball milling for 2 h, the mixture was heated in air up to 1273 K for 24 h. The obtained powders were pressed into pellets of about 2 mm thickness and 13 mm diameter and then sintered at 1573 K.

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Finally, these pellets were slowly cooled down to room temperature. Phase purity and homogeneity were determined by powder X-ray diffraction at room temperature. Magnetization measurements versus temperature in the range 80–350 K and versus applied magnetic field up to 20 Oe were carried out using a Vibrating Sample Magnetometer (VSM). The MCE was calculated from the magnetization measurements versus applied magnetic field up to 15 kOe at various temperatures.

### 3. Results

The analysis of X-ray pattern confirms the single phase of  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{M}_{0.2}\text{MnO}_3$  ( $M=\text{Na, Li, K and Ag}$ ) with orthorhombic structure (space group  $pnma$ ). No detectable second phase was found. The temperature dependence of magnetization of  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{Na}_{0.2}\text{MnO}_3$  measured in the magnetic field of 20 Oe displays large divergence between zero-field cooled (ZFC) and field cooled magnetization (FC) curves below 285 K (Fig. 1), which is indicative of magnetic glassy behavior [11]. The divergence between ZFC and FC could also result from an anisotropy effect [12], and competition between ferromagnetic and antiferromagnetic coupling. Spin glasses as a result of competing ferromagnetic double exchange and antiferromagnetic super-exchange interactions are not new [13,14]. The divergence behavior can be interpreted by facts that at low temperature the antiferromagnetic phase is more stable while application of a magnetic field tends to stabilize the ferromagnetic phase. However, there is no charge-order transition found, which has been extensively reported in half doped PSMO systems [15–17]. Tomioka et al. [13] showed that the charge order becomes actively favorable for doped electrons to get localized and crystallized. are larger Tolerance factors of 0.95 (Na), 0.97 (K) and 0.95 (Ag) are larger compared to 0.93 of  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{M}_{0.2}\text{MnO}_3$ . [18]. In this case double exchange interaction is enhanced, subsequently with an increase in the transfer of  $e_g$  holes (electrons) which also may gain because of metallicity of the monovalent element. Thus it suppresses the charge order.

The Curie temperatures ( $T_C$ ) are determined at the inflection point of  $dM/dT$  curves of the samples. The para-ferromagnetic transition temperatures are 285, 290, 290 and 290 K for Na, Li, K and Ag doped samples respectively. In the double exchange mechanism,  $T_C$  was estimated [19] as  $T_C \sim J \sim t_{dp}^2 \sim S_{dp}^2 \sim \cos^2 \theta$  ( $J$ : effective exchange between adjacent Mn ions;  $t_{dp}^2$ : Mnd-O2p transfer integral;  $S_{dp}^2$ : overlap and  $\theta$ : angle of Mn-O). Thus almost the same values of  $T_C$  could be ascribed to the similar electronic

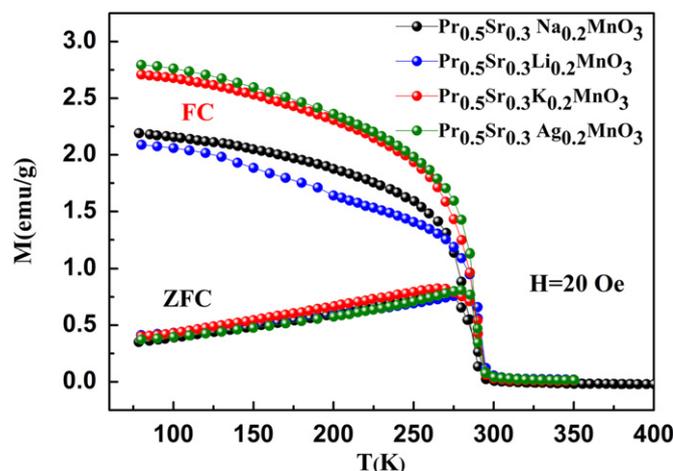


Fig. 1. Temperature dependence of zero-field cooled (ZFC) and field cooled (FC) magnetization curves measured at 20 Oe for  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{M}_{0.2}\text{MnO}_3$  (Na, Li, K and Ag).

configuration and tolerance factor doped at the A-site of manganites. The tolerance factor approaching 1 increases the angle of Mn-O which is beneficial to get a high value of Curie temperature. Das and Dey [8], explained that the increase in the  $T_C$  was from the larger  $\text{K}^{1+}$  ion than  $\text{La}^{3+}$  ion but in our case  $\text{Li}^{1+}$  ion (ionic radii  $\sim 0.92 \text{ \AA}$ ) is smaller than  $\text{Pr}^{3+}$  (ionic radii  $\sim 1.126 \text{ \AA}$ ). Therefore it is suggested that the similar electronic configuration may mainly give rise to the observed increase in the phase transition temperature from 161 K [5] to room temperature. The magnetic entropy change  $\Delta S_M$  which is associated with the MCE could be calculated from isothermal magnetization data (Fig. 2) using the thermodynamic Maxwell relation

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

where  $H_{\max}$  is the maximum value of the applied magnetic field. Thus the maximum values of  $\Delta S_M$  are 1.8, 2.2, 1.6 and 2.1 J/kg K for Na, Li, K and Ag, respectively, in the magnetic field change of 15 kOe (Fig. 3). The magnetic entropy change of 2.2 J/kg K for  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{Li}_{0.2}\text{MnO}_3$  is about 52% of that of pure Gd, [20] and is larger than the  $\Delta S_M$  values of  $\text{Pr}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$  [21,22]. For common household, automotive, and practical magnetic cooling applications in general the magnetic fields induced by permanent magnets are about 20 kOe [23]. Consequently our materials with large magnetic entropy changes generated by low magnetic field are beneficial for practical applications. The relative cooling power (RCP) is the most important parameter to determine the cooling efficiency or the usefulness of a magnetic refrigerant material. The RCP is defined as

$$\text{RCP} = |\Delta S_M| \delta T_{\text{FWHM}} \quad (2)$$

where  $\delta T_{\text{FWHM}}$  is the full width at the half maximum value of  $\Delta S_M$  versus  $T$  curves.  $\delta T_{\text{FWHM}}$  is relatively large, reaching 27 and 45 K for Li and K doped samples respectively. The wide temperature range for  $\delta T_{\text{FWHM}}$  gives rise to a high value of RCP. In general, better the RCP values the better the materials for magnetic refrigeration because materials with higher RCP would support the transport of a greater amount of heat in a practical refrigerator. In our work, the RCP values reach 58.9, 59.3, 69.6 and 54.6 J/kg for Na, Li, K and Ag doped samples respectively. These values are comparable to those reported for other manganites [2], and high enough to propose our manganite materials as active magnetic refrigerants working around room temperature. The

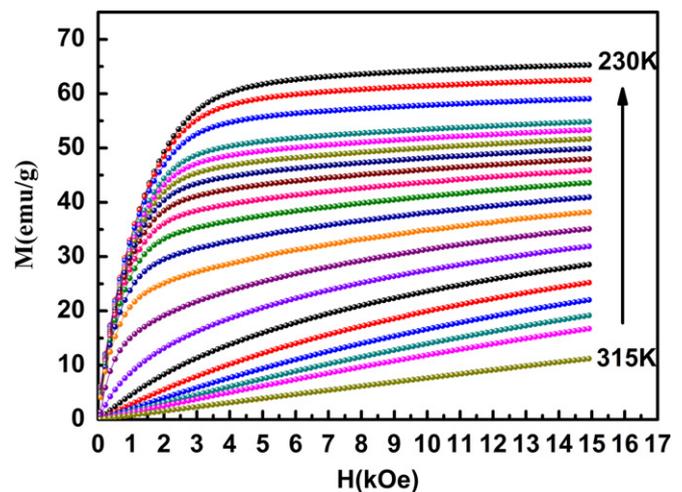


Fig. 2. Isothermal magnetization curves of  $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{Li}_{0.2}\text{MnO}_3$  measured at different temperatures.

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