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Synthesis, characterisation and study of magnetocaloric properties of $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$

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Abstract. Polycrystalline perovskite-type manganite $La_{0.65}Sr_{0.25}K_{0.1}Mn_xV_{1-x}O_3$ were prepared by sol-gel method. An X-ray diffraction at room temperature indicated that all samples have a single phase with R-3c space group. Magnetic properties and Curie temperature are measured by superconducting quantum interference device. Magnetization as a function of temperature shows that all samples exhibit a paramagnetic-ferromagnetic phase transition at the Curie temperature. The Curie temperature of samples was increased from 342 K for x=0.00 to 351 K for x=0.15. The magnetic entropy change deduced from the measured magnetization data using Maxwell relation. The maximum magnetic entropy change $-\Delta S_M$ corresponding to a 1 T magnetic field variation was found to be 1.0 J/kg K for x=0.05. The style of phase transition of the manganite was distinguished by Banerjee criteria.

1. Introduction

Recently, magnetocaloric materials have received increasing attention as materials for application in magnetic refrigeration technology. This is because magnetic refrigeration is a promising cooling technology due to its chemical stability, environmental friendliness, low cost and higher cooling efficiency compared to conventional refrigeration. This technique is ground on the magnetocaloric effect (MCE) which is an inherent characteristic of magnetic materials[1, 2]. MCE can be characterized by the adiabatic temperature change (ΔT_{ad}), and the isothermal entropy change (ΔS_M) which can be calculated as functions of magnetic field and temperatures[3]. Thus, further development of magnetic refrigeration needs to find out magnetic materials with large MCE.

Perovskite manganites with general formula $R_{1-x}A_xMnO_3$ (R and A are rare-earth and divalent-alkaline elements, respectively) are perceived as attractive materials. This is due to their large magnetocaloric effects (MCE) can be observed near the magnetic phase transition temperature[3, 4]. These properties can be attributed to the double exchange interaction presented by Zener[5].The magnetic coupling between Mn^{4+} and Mn^{3+} ions results from the motion of e_g electrons between two partially filled d-orbitals with strong on-site Hund's coupling in addition to dynamic Jahn-Teller distortions generated from strong electron-phonon coupling [6]. The study of doping effects on the Mn-site by other elements is very important. These materials have shown possibilities, but the narrow temperature range near T_C and the requirement of large magnetic field of several tesla limits the applications [7-9]. The Sr doped system $La_{1-x}Sr_xMnO_3$ was found to exhibit a large MCE and other interesting properties [10, 11]. Several investigations were carried out to understand the MCE of $R_{1-x}A_xMnO3$[3, 12]. However, the magnetocaloric properties doping at Mn-site in $R_{1-x}A_xMnO_3$ have not been investigated so far. Nisha et al[13] found that increasing vanadium concentration could achieve

highest entropy change for $La_{0.67}Ca_{0.33}Mn_{1-x}V_xO_3$ which encourages us to analyze the physical properties of vanadium substitution in $La_{0.65}Sr_{0.25}K_{0.1}MnO_3$.

This study aims to investigate the effect of vanadium substituted on structure, magnetic and magnetocaloric properties in the polycrystalline $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$ manganite. It reported a compound showing a large MCE near room temperature.

2. Experimental

A polycrystalline manganite $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$ was prepared by sol-gel technique[14]. The structures of the samples were characterized by X-ray powder diffraction (XRD, X' Pert Pro) with Cu Kα radiation. The magnetic properties were measured by superconducting quantum interference device (SQUID, MPMS XL-7).

3. Results and discussions

3.1 Structural study

The powder X-ray diffraction patterns (Fig. 1) indicated that $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$ samples exhibited a single-phase perovskite structure without a detectable secondary phase. Detailed analyses of the structure based on the standard PDF card (PDF#54-1195) in MDI Jade 6.0 revealed that all the samples were single phase without any impurity peaks (space group: R-3c)[15]. A shifting trend towards higher 2θ value can be observed on the XRD peaks (the inset of Fig.1) upon increasing the vanadium content.

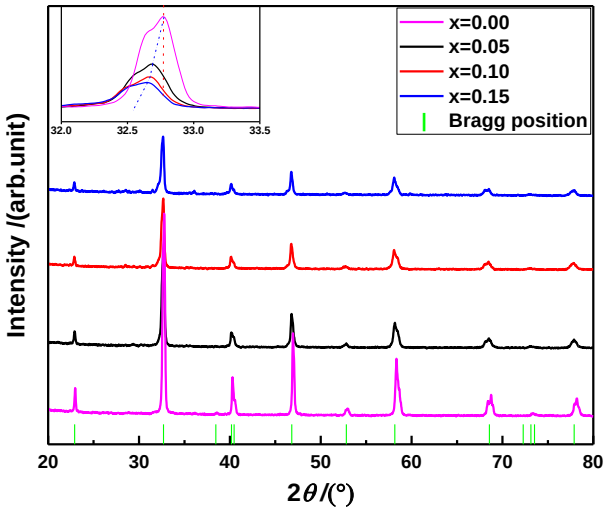

Fig. 1 XRD patterns at room temperature of $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$

3.2 Magnetic and magnetocaloric properties

Fig.2 shows the temperature dependence of magnetization in the field cooling process and the dM/dT curves for $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$ samples in the magnetic field of 0.1 T. A transitionfrom paramagnetic to ferromagnetic (PM-FM) can be clearly observed. The Curie temperature T_C can be defined as the minimum of the derivatives of M with respect to T. The values of T_C are found to be 342 K, 342 K，344 K and 351 K for x=0.00，0.05, 0.10 and 0.15, respectively. The T_C present a non-significant increase with increasing vanadium content. This can be explained by the increase of vanadium changed some amount of bands in Mn^{3+}-O-Mn^{4+}, so the enhance of double exchange interaction between Mn^{3+} and Mn^{4+} induced an increase in PM-FM transition temperature.

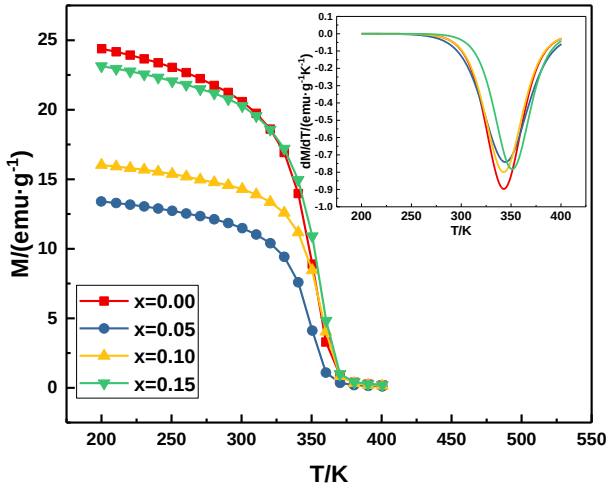

Fig. 2 Temperature dependence of the magnetization measured at H=0.1 T for $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$ (x=0.00, 0.05, 0.10 and 0.15) compounds. The inset indicates the dM/dT (T) curves used to determine T_C.

The isothermal magnetization of $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$ as a function of applied magnetic field at different temperatures around *Tc* is shown in Fig.3. Obviously, the magnetization *M* increases sharply under 0.2 T and tends to saturates above 0.5 T. With decreasing temperature, the saturation magnetization reaches higher values.

To get a deeper insight into the type of magnetic phase transition, the magnetic entropy change as a function of temperature can be theoretically calculated by the formula based on Landau theory [16]:

$$G(M, T)=G_0+1/2AM^2+1/4BM^4-MH \quad (1)$$

Where *A* and *B* are the temperature dependent parameters known as Landau coefficients. From the equilibrium condition, $\partial G/\partial M=0$, the equation of magnetization can be described as follows[16]:

$$H/M=A+BM^2 \quad (2)$$

According to Banerjee's criteria [17, 18], a negative or positive slope of the *H/M* versus M^2 curve implies corresponds to the first or second order magnetic phase transition, respectively. The right side of Fig.3 shows the M^2 versus *H/M* plots of isotherms around T_C. Clearly, the Arrott plots obtained for all samples display positive slopes, which confirms a second-order FM to PM phase transition occurs.

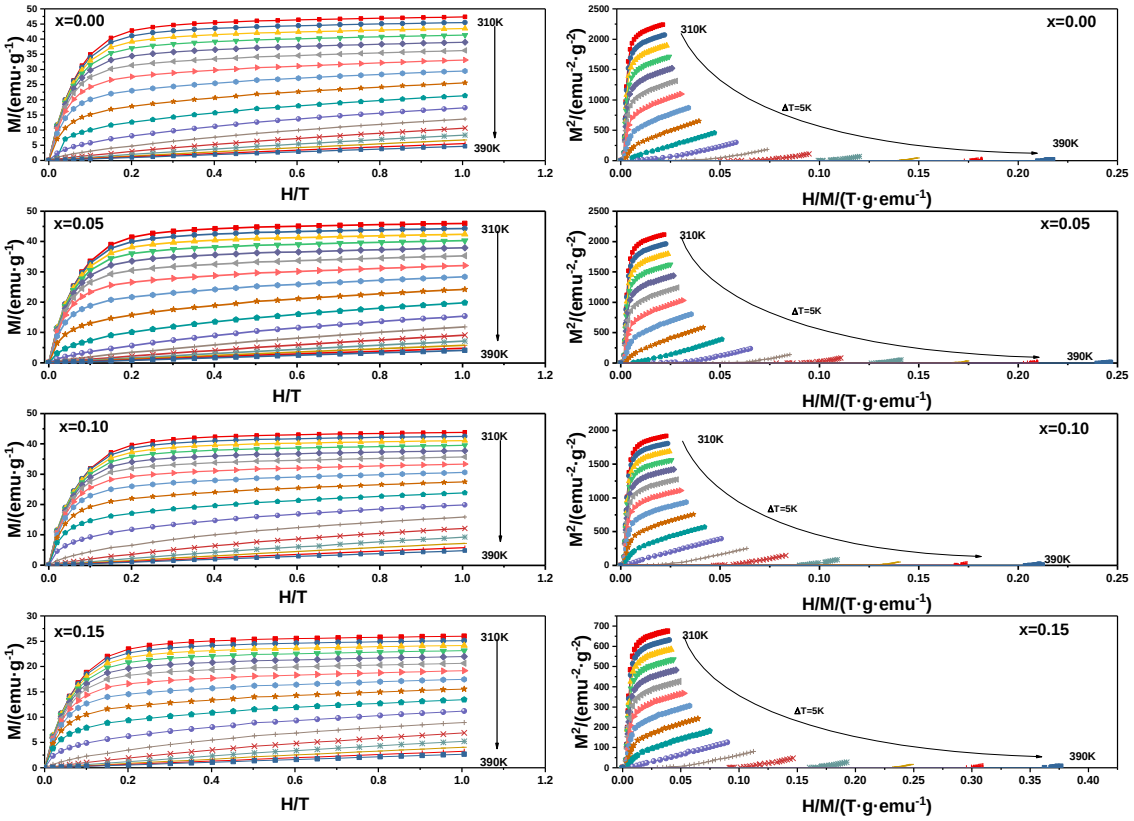

Fig.3 Isothermal magnetization of $La_{0.65}Sr_{0.25}K_{0.1}Mn_xV_{1-x}O_3$ (x=0.00, 0.05, 0.10 and 0.15) as a function of applied magnetic field at different temperatures around T_C and corresponding Arrott plots.

To estimate the magnetocaloric effect, the ΔS_M can be calculated by thermodynamic Maxwell's relations:

$$\Delta S_M(T,H) = \Delta S_M(T,H_1) - \Delta S_M(T,H_2) = \int_{H_1}^{H_2} \left(\frac{\partial M}{\partial T}\right) dH \qquad (3)$$

Where M_i and M_{i+1} are the experimental values of magnetization measured at temperatures T_i and T_{i+1}, respectively, under a magnetic field H_i. Fig.4 presents the magnetic entropy change of $La_{0.65}Sr_{0.25}K_{0.1}Mn1\text{-}_xV_xO_3$ (x=0.00, 0.05, 0.10 and 0.15) under different external fields. We found that our $-\Delta S_M$, 1.0 kg^{-1} K^{-1} for 1 T which is large compared to un-doped sample and other manganites [19, 20]. Furthermore, the maximum magnetic entropy change was increased gradually with increasing applied magnetic field as shown in Fig 7. These results revealed that our sample shows large magnetocaloric effect to be used as magnetic refrigerants.

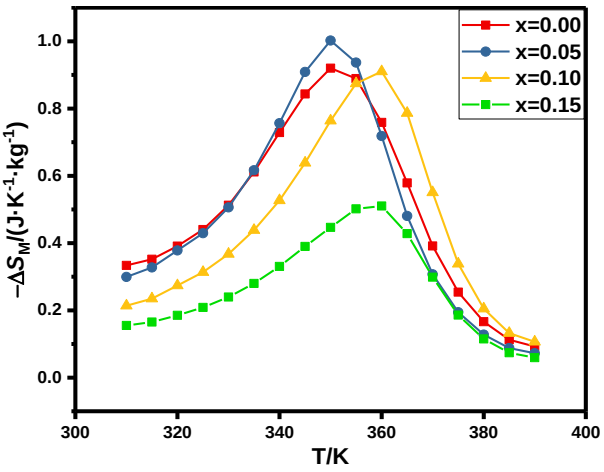

Fig. 4. Isothermal entropy change as a function of temperature with a field change of 1.0 T for $La_{0.65}Sr_{0.25}K_{0.1}Mn_{1-x}V_xO_3$ (x=0.00, 0.05, 0.10 and 0.15) samples.

Besides, the other important parameter, the change of heat capacity $\Delta C_{P,H}$ associated with a magnetic field variation from 0 to $\mu_0 H$ can be calculated from the ΔS_M data by the following relation[6]:

$$\Delta C_{P,H}=C_P\ (T,\ \mu_0 H)-\Delta C_P\ (T,\ 0)= -T\frac{\partial(\Delta S_M\ (T,\mu_0 H))}{\partial T} \quad (5)$$

As a representative of samples, the temperature dependence of the change of the $\Delta C_{P,H}$ fordifferent field variations of $La_{0.65}Sr_{0.25}K_{0.1}Mn_{0.95}V_{0.05}O_3$. We can see that the value of $\Delta C_{P,H}$ changes sharply from positive to negative around the Curie temperature. Besides, at $T > T_C$, $\Delta C_{P,H} > 0$ and at $T < T_C$ $\Delta C_{P,H} < 0$. The two parts contributed to the total specific heat. [21]

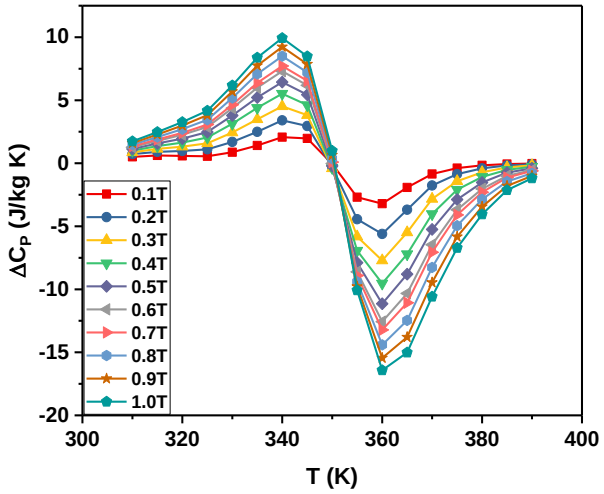

Fig. 5 Heat capacity change $\Delta C_{P,H}$ as a function of temperature for $La_{0.65}Sr_{0.25}K_{0.1}Mn_{0.95}V_{0.05}O_3$ in different applied magnetic field variatios.

To determine the cooling efficiency of magnetic refrigeration, the relative cooling power (*RCP*) is another effective parameter. It corresponds to the amount of heat transfer between the hot and cold sinks during one ideal refrigeration cycle. *RCP* can be calculated using the relation[22]:

$$RCP = |\Delta S_M^{max}| \times \delta_{FWHM} \quad (4)$$

Where δT_{FWHM} is the full-width at half maximum of magnetic entropy change$|\Delta S_M^{max}|$. The data of *RCP* under different magnetic fields can be calculated according to the Fig. 4. The values of *RCP* were found to be 38.3, 35.3, 32.9 and 20.4 J/kg, respectively. This result is interesting enough in a low

magnetic field, compared to those observed in other materials[4]. Therefore, our material can be considered as a prospective substance to be used in magnetic refrigeration.

4. Conclusion

In summary, a detailed investigation of magnetic and magnetocaloric properties of polycrystalli ne samples $La_{0.65}Sr_{0.25}K_{0.1}Mn_xV_{1-x}O_3$ (x=0.00, 0.05, 0.10 and 0.15) synthesized by sol-gel meth od have been carried out. The XRD analysis confirmed that our samples crystallized in a rho mbic structure with R-3c space group. The Curie temperature was increased from 342 K to 35 1 K with the increase of V content. The regular variations of Curie temperature and magnetic entropy change have been found by magnetization measurements. The high values of relative cooling power make these materials attractive for potential application in a low magnetic field. Using Banerjee criteria, the phase transition of the samples were determined to be the secon d-order.

Acknowledgments

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