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Effect of Nb doping at Mn site on thermal expansion of $Pr_{0.7}Sr_{0.3}MnO_3$

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ABSTRACT

In this study we present results on effect of Nb doping on thermal expansion of $Pr_{0.7}Sr_{0.3}MnO_3$. Thermal expansion measurements were done using three terminal capacitance method. The pure sample shows a jump at the insulator–metal (I-M) transition temperature, and with Nb doping, a fourfold decrease in the jump is found. Since thermal expansion is a bulk property, this suggests that the dopants are not in the form of local clusters; rather they are distributed uniformly throughout the sample. Temperature variation of Gruniesen ratio α/C_P shows that for temperatures below I–M transition, the ratio is weakly dependent on temperature. Pressure dependence on the transition temperature, dT_P/dP and jump in compressibility, $\Delta\beta$, of these samples has been estimated using well-known Ehrenfest equations. The present results are in fairly good agreement with those reported in the literature.

1. Introduction

During last two decades, perovskite manganites with chemical formula, ABO_3, (where A is a trivalent rare-earth ion or divalent alkali earth-ion and B is trivalent transition metal ion), have been the subject of intense research essentially because of the fascinating underlying physics showing noticeable colossal magneto-resistance (CMR) effect and the anticipated multifunctional and advanced applications for the next generation electronics [1]. The discovery of large MR observed in manganites with general formula $R_{1-x}A_xMnO_3$ has generated great interest among the researchers to understand the intricate relationships between lattice distortion, magnetism, and thermodynamic properties of pure and doped manganites. In particular manganites like $R_{1-x}A_xMnO_3$ are excellent candidates for sensor applications, bolometers, magnetic refrigeration and read head devices.

There are several reports on the electrical and thermal properties of doped $Pr_{0.7}Sr_{0.3}MnO_3$ (PSMO), $Pr_{2/3}Ba_{1/3}MnO_3$ (PBMO) and $La_{2/3}Ba_{1/3}MnO_3$ (LBMO) manganites [2–9]. PSMO is, in fact, one of the important CMR materials having its insulator–metal transition temperature near room temperature. Electrical and thermal studies provide valuable information like the nature of charge carriers and scattering mechanism. However, there are relatively few reports on thermal expansion studies on manganites in the literature [10–12]. In particular, thermal expansion of solids provides a very useful tool to study the phase transitions and lattice dynamics. In fact, the anomalous responses of thermal expansion and specific heat measurements during a second order phase transition would yield information about the pressure dependence of transition temperature through Ehrenfest relation which is otherwise difficult to measure. Despite intense studies, a comprehensive understanding of the conduction mechanism is still elusive. In order to understand the physics of these materials, one either dope some elements at the rare-earth site which indirectly modifies the conduction mechanism or one can directly tailor it by doping at the Mn-site.

Recently, we reported the structural, electrical and thermal measurements on Nb^{+5} – ion (using Nb_2O_5) doped $Pr_{0.7}Sr_{0.3}MnO_3$ (PSMO) system [13]. The rationale for choosing Nb is that it has the inert shell electronic configuration of Kr and we anticipate that it will not produce extra magnetic coupling. In addition, we also expect that such a doping may modify Mn^{+3}/Mn^{+4} ratio. Such a study revealed that the I–M transition occurs around 280 K and the observed absence of grain boundary effects arise from the cationic mismatch in this system. To the best of our knowledge, there is no report on thermal expansion measurements of these compounds so far. In the present study, we report the effect of Nb doping on thermal expansion of PSMO system. It is found that the pure sample shows a pronounced jump at the insulator–metal (I–M) transition temperature, while a fourfold decrease in the jump is

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observed with only 1% Nb doping. Furthermore, by applying Ehrenfest equations, we have estimated the pressure dependence of transition temperature and the jumps in compressibility of these manganites.

2. Experimental techniques

Series of samples with nominal composition of $Pr_{0.7}Sr_{0.3}Mn_{1-x}Nb_xO_3$ (x=0,1%) were prepared by conventional solid state reaction method. The details of sample preparation along with the electrical and thermal transport properties are reported elsewhere [13]. The length change and thermal expansion measurements were performed using a capacitance dilatometer. In such a dilatometer, one of the plates is attached to the sample whose thermal expansion coefficient is to be measured. The other plate is thermally isolated from the first plate. When the sample is heated, the distance between the plates changes and hence one can measure the changes in capacitance. In the present setup, the sample is mounted on a copper base using a thermal epoxy (Stycast 2850 FT Black). The sample carries a capacitance plate which is about 1 mm thick and 5 mm in diameter. The relative change in length was measured by measuring capacitance using a single frequency ultra-precision capacitance bridge, Andeen-Hagerling 2550A.

3. Results and discussions

Fig. 1 shows the behavior of relative length change, $\Delta L/L$, as a function of temperature for the pure sample of $Pr_{0.7}Sr_{0.3}MnO_3$ (see the inset). One can observe a hump at the transition temperature. Using the data of length changes, coefficient of thermal expansion for the samples was calculated. Fig. 1 also depicts the temperature dependent thermal expansion, α for the pure sample. A sharp jump in thermal expansion, responding to the onset of second order phase transition, is clearly observed. It should be mentioned that a similar trend was seen in the specific heat, C_P, where a sharp discontinuity was observed around the transition temperature [13]. Fig. 2 depicts the variation of length change and coefficient

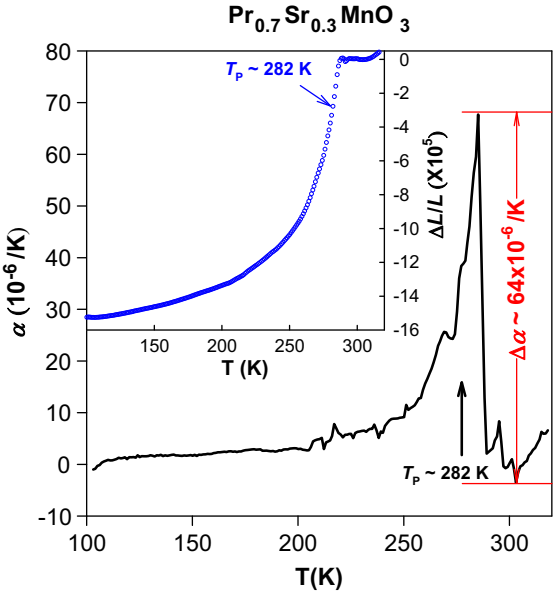

Fig. 1. (Color online) Thermal expansion coefficient as a function of temperature for pure sample. Inset: Temperature dependence of the relative length changes, $\Delta L/L$, of $Pr_{0.7}Sr_{0.3}MnO_3$.

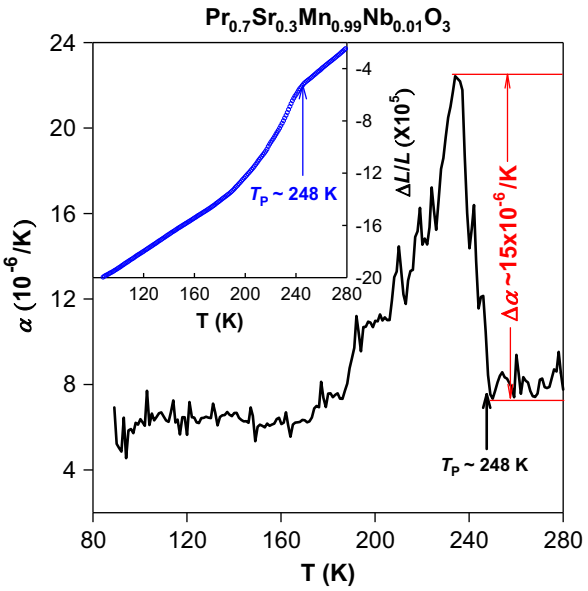

Fig. 2. (Color online) Thermal expansion coefficient as a function of temperature for 1% Nb doped sample. Inset: Temperature dependence of the relative length changes, $\Delta L/L$, of $Pr_{0.7}Sr_{0.3}Mn_{0.99}Nb_{0.01}O_3$.

of thermal expansion for 1% Nb doped sample of $Pr_{0.7}Sr_{0.3}MnO_3$. For the doped sample we observe that the hump in length change at the transition drastically decreases, however, the expected jump in thermal expansion at the transition temperature is still well evident. Likewise, a specific heat jump was also observed for the 1% Nb doped sample during the transition [13].

It is well-known that the transition to a magnetically ordered phase in manganites (with the removal of Jahn Teller distortion) is accompanied by contraction of the lattice [11]. Using extrapolation of the experimental data of relative length change before and after magnetic phase transition, we have estimated the spontaneous magnetostriction for the pure sample of $Pr_{0.7}Sr_{0.3}MnO_3$ to be 2.5×10^{-5} and it is found to be decreased to 0.8×10^{-5} for 1% Nb doped sample. For comparison, the spontaneous magnetostriction of about 1.58×10^{-5} is observed for $La_{0.8}Ag_{0.15}MnO_3$ compounds [11]. For $RE_{1-x}Sr_xMnO_3$ (RE=Sm, Nd) compounds its value is about 5×10^{-4} [14]. Thus one can see that the present results match well with those reported in literature.

The Grüneisen parameter, γ, describes the effect of change in volume of a crystal lattice on its vibrational properties is given by

$$\gamma = \frac{\alpha K}{\rho C_P} \tag{1}$$

where K denotes the adiabatic bulk modulus, α is thermal expansion coefficient, ρ is the density and C_P is the specific heat at constant pressure. In the present investigation, we have not performed bulk modulus measurements, however we can use the fact that γ can be taken as a fraction of α/C_P. Fig. 3 shows the temperature dependent Gruneisen ratio in terms of α/C_P. For the pure sample of $Pr_{0.7}Sr_{0.3}MnO_3$, it is clearly seen that the Gruniesen ratio exhibits a jump around the transition temperature. It is further observed that the ratio has a weak temperature dependence below the transition temperature. This suggests that only phonon degree of freedom is relevant in this temperature range [14]. For the Nb doped sample, we also observe a jump in the Gruniesen ratio (see Fig. 3). However, a stronger temperature dependence below transition temperature is noticed. The jump in Gruniesen ration also decreases with Nb doping. For the pure sample of $Pr_{0.7}Sr_{0.3}MnO_3$, the jump in the ratio is about

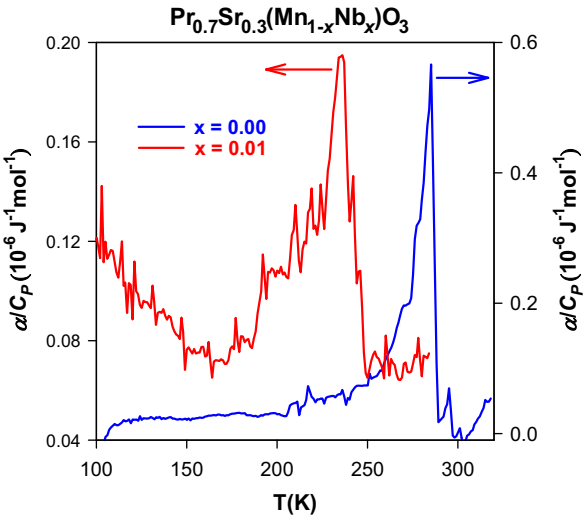

Fig. 3. (Color online) Temperature dependence of Gruneisen ratio α/C_P for $Pr_{0.7}Sr_{0.3}Mn_{1-x}Nb_xO_3$ ($x=0$, 0.01) samples.

$0.5\times10^{-6}\,J^{-1}\,mol^{-1}$; while it decreases to $0.12\times10^{-6}\,J^{-1}\,mol^{-1}$ for the 1% Nb doped sample.

The jumps in specific heat and thermal expansion are related via Ehrenfest relation at a second order transition which is given by

$$\Delta\alpha=\frac{1}{3V}\left(\frac{\Delta C_P}{T_0}\right)\left(\frac{dT_P}{dP}\right) \tag{2}$$

The importance of the above relation lies in the fact that one can estimate the pressure dependence on transition temperature, dT_P/dP. Usually the accurate measurements of dT_P/dP are difficult and hence Eq. (1) can provide an alternative way to obtain dT_P/dP. The estimated jump in thermal expansion for pure sample of $Pr_{0.7}Sr_{0.3}MnO_3$ was observed to be about 64×10^{-6}/K and with 1% Nb doping, it is decreases to 15×10^{-6}/K. It is noted that with only 1% Nb dopant, the thermal expansion jump decreases by as much as a factor of 4. This suggests that the dopants are distributed uniformly throughout the sample and not as local clusters, as thermal expansion is a bulk thermodynamic property. From Ref. [13], the value of specific heat jump is 22.51 J/mol K for pure sample and it decreases to 10.32 J/mol K for the sample with 1% Nb doping. Substituting the experimental values of ΔC_P and $\Delta\alpha$ into Eq. (2), we obtain the pressure dependence of transition temperature dT_P/dP of 24 K/GPa and 11 K/GPa for pure and 1% Nb doped $Pr_{0.7}Sr_{0.3}MnO_3$ samples, respectively. These results are in good agreement with the experimental data of dT_P/dP for similar compounds as reported in the literature [15]. Another thermodynamic discontinuity which is seen in a second order phase transition is the jump in compressibility, $\Delta\beta$, which is given by another Ehrenfest equation given below

$$\Delta\beta=\frac{\Delta\alpha}{3}\left(\frac{dT_P}{dP}\right) \tag{3}$$

Application of this equation provides an indirect method to estimate the jump in compressibility. We thus estimated $\Delta\beta\sim5.15\times10^{-3}$/GPa for the pure sample of $Pr_{0.7}Sr_{0.3}MnO_3$, while it decreases to 0.58×10^{-3}/GPa with 1% Nb doping. To the best of our knowledge, no direct measurements of compressibility have been carried out on these manganites.

4. Conclusions

We have carried out an investigation of the effect of Nb doping in $Pr_{0.7}Sr_{0.3}MnO_3$ via thermal expansion measurements. It is seen that a pronounced jump in thermal expansion at the transition temperature confirms the second-order nature of the phase transition. It is also seen that the jump decreases by a factor of about 4 when only 1% Nb is doped at Mn site. Such a finding suggests that the added impurity is uniformly distributed throughout the sample. By using Ehrenfest equations, we have estimated the pressure dependence of transition temperature to be about 24 K/GPa and 11 K/GPa for pure and 1% Nb doped $Pr_{0.7}Sr_{0.3}MnO_3$ samples, respectively. In addition, the value of jump in compressibility $\Delta\beta\sim5.15\times10^{-3}$/GPa was obtained for $Pr_{0.7}Sr_{0.3}MnO_3$, that decreases by almost an order of magnitude with 1% Nb doping.

Acknowledgments

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