



MAGNETO-ELECTRIC PROPERTIES AND MAGNETIC ENTROPY CHANGE IN PEROVSKITE



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ABSTRACT

The ceramic samples of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x=0; 0.05; 0.1; 0.2$ and 0.3) were synthesized by the conventional solid state reaction method. Their electric, magnetic and magnetocaloric properties have been investigated. The transition temperature declines and a significant influence on the width of the ferro-paramagnetic phase transition is observed as increasing Ti concentration. Moreover, the sign of spin-glass is expected to exist in the high concentration samples. For fully replacing Ti^{4+} for Mn^{4+} , the canted spin state is formed. The substitution Ti for Mn increases resistivity quickly and the insulating-metallic transition temperature shifts toward lower temperature. For $x > 0.1$ samples, the insulating state is observed even in ferromagnetic phase. The substitution Ti shifts the CME to room temperature while almost persists the value of entropy change and improves the relative cooling power is improved. These properties could be explained in term of DE interaction and phase separation phenomenon.

KEYWORDS

Perovskite, manganite, magnetocaloric, magnetic entropy change.

1. Introduction

Much attention has been devoted to the hole-doped manganites $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ (Ln: lanthanides, A: alkali elements), systems that are strongly attractive to research and technology due to their rich physics and potential applications such as colossal magneto-resistance, magnetocaloric. The electro-magnetic properties have been explained by double exchange interaction that has been suggested by Zener [1]. The strongest magnetic properties are often detected at the concentration of $x=0.3$ according to the fraction of $\text{Mn}^{4+}/\text{Mn}^{3+}$ is 3/7. Substitution some ions for ion of Mn in $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ has been interested because of interesting properties that could be applied especially the low-field magnetoresistance effect [2-4]. Studies partly replacing A site have been carried out and the phase diagram also presented. Samples could be ferromagnetic-metallic, paramagnetic-insulating, ferromagnetic-insulating or spin glass - insulating depending on the ratio of $\text{B}^{4+}/\text{B}^{3+}$ caused by substitution as well as extrinsic physical conditions [5-7]. Substitution B by other elements to explore the interaction between substituted ions and Mn or Co ions as well as electro-magnetic effects has generated remarkable issues especially colossal magnetoresistance (CMR) effect [5,8]. In this study, Ti is collected to substitute for Mn in the mother compound of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ due to the following reasons: (i) Ti ion always exist the state of Ti^{4+} in the structure of perovskite. This leads to stability the concentration of Mn^{3+} . As a result, the double exchange (DE) interaction between Mn^{3+} and Mn^{4+} at the site located by Ti^{4+} and (ii) Ti^{4+} is non-magnetic ion. Thus, the influence of magnetic disturbance of substituted ions on magnetic property of sample is expected to be restricted.

2. Experiment

The polycrystalline compounds of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x=0; 0.05; 0.1; 0.2$ and 0.3) have been synthesized by standard solid state reaction method with the sintered temperature of 1370°C within 48 hours. Magnetic and magnetization measurements were performed in a Quantum Design MPMS SQUID magnetometer. The temperature dependence of the dc resistivity was measured by conventional four probe method under high vacuum conditions, cooling down the samples in the range $30 - 300$ K using a Keithley 2000 and 2001 digital multimeters.

3. Results and discussion

3.1. The structural properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$

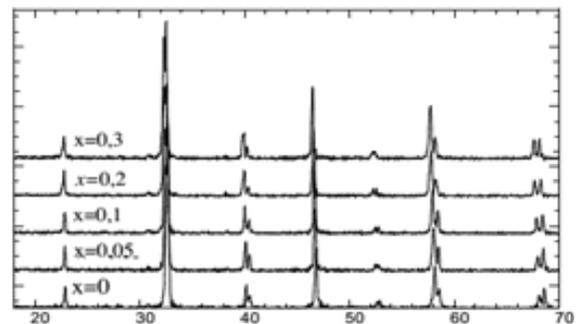


Fig. 1. XRD patterns of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ samples

Figure 1 demonstrates the room-temperature x-ray diffraction of the samples. It is clear that the samples are single phase in structure. It also shows the crystalline structure belong to perovskite rhombohedral (space group) structures. The previous studies show that the substitution Mn^{4+} ions by Ti^{4+} ions increases the distance of Mn-O and the volume of unit cells. Contrary, the relational corner of Mn-O-Mn decreases as increasing Ti concentration [9-12]. However, there is not any change in structure up to 30% Mn ions that are substituted by Ti ions [9], [10]. These results could imply that Ti^{4+} ions locate in the crystalline structure and cause the change of tolerance factor τ from 0,928 to 0,921 as increasing Ti concentration from $x = 0$ to $x = 0,2$ [13]

3.2. The magnetic properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$

Figure 2 presents the temperature dependence of magnetization of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ ($x = 0 - 0.1$) samples in the modes of field-cooled (FC) and zero-field cooled (ZFC) ($H = 100$ Oe). It is clear that phase transition temperature of ferro-paramagnetic is reduced as increasing Ti concentration. It is $\sim 10.4\text{K}/1\%$ ion Mn substituted. This figure is higher than that of substitution Al and similar to the previous works [14-17].

The DE interaction is collapsed at the site that Mn^{4+} is replaced by Ti^{4+} because Ti^{4+} is non-magnetic ion. Thus, similar to substitution Al [18], the diluted magnetic net effect will generate. In case of Al substitution, Al^{3+} ion is expected to be replaced for Mn^{3+} ion. However, in this case Ti^{4+} ion replaces directly for Mn^{4+} ion. This substitution will not

change density of Zener electron. Moreover, radius of Ti^{4+} ion (0.605 Å) is larger than Mn^{4+} ion (0.540 Å). This leads to increase the average distance between Mn and O (Mn-O) [15], [16] and to reduce the corner of Mn-O-Mn [16]. These effects are expected to deplete the DE interaction. Consequently, the ferro-paramagnetic phase transition temperature is reduced drastically. This could be explained by the drastic decrease of the Mn^{4+}/Mn^{3+} ratio from the optimal ratio of 3/7 (in the case of $x = 0.1$, the ratio is 2/7 only).

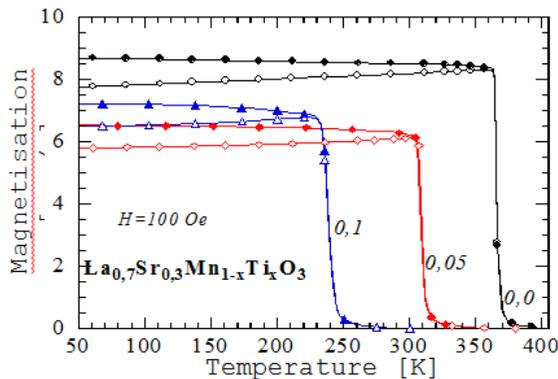


Fig. 2. The temperature dependence of magnetization of $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ ($x=0,0,1$) measured in the magnetic field of 100 Oe in FC (empty) and ZFC (solid) modes.

The difference between the $M_{FC}(T)$ and $M_{ZFC}(T)$ curves in ferromagnetic phase is similar to other conventional magnetic materials measured in low magnet. This difference and form of $M_{ZFC}(T)$ curve are explained by: (i) competition between external field and anisotropic field and (ii) the change of anisotropic field and spontaneous magnetization as temperature. This phenomenon will be clearer in the low applied field. It will vanish in a high enough external magnet [18].

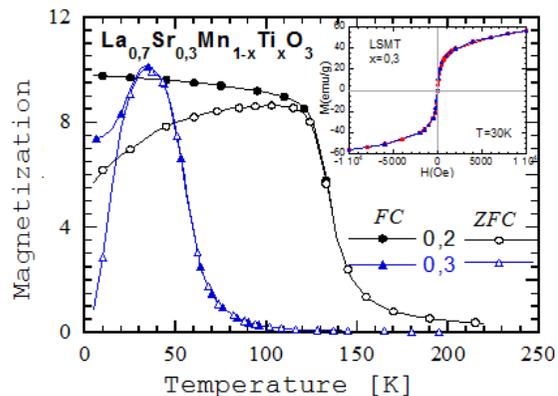


Fig. 3. The temperature dependence of the samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ ($x=0.2-0.3$) measured in the applied field of 100 Oe in FC and ZFC modes. The insert presents the $M(H)$ curve of $x=0.3$ sample.

Figure 3 shows the temperature dependence of the magnetization of $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ samples for the components of $x = 0.2 - 0.3$. Transition temperature continues to decline accompanied by a significant influence on the width of the ferro-paramagnetic phase transition as increasing the concentration of paramagnetic Ti. The extension of the width of the transition region has been observed in preview studies if Mn^{3+} is substituted by other ions with a higher concentration [19-21].

In case of $x = 0.3$ compound, Mn^{4+} should be no longer be-

cause of existence of Ti^{4+} then this sample is expected to be antiferromagnetic. Although the figure 3 implies an antiferromagnetic transition at temperature of ~ 50K, difference between $M_{FC}(T)$ and $M_{ZFC}(T)$ curves in this poly-crystal under T_C suggests that this transition is not formal antiferromagnetic transition and it behaves ferro-interaction. This could be confirmed by the $M(H)$ inserted in the figure 3. The $M(T)$ curve suggests a sign of spin state instead of long range magnetic order in the sample of $x = 0.3$. It is similar to what observed in the samples of $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$ [22], [23] as well as other spin-glass samples. However, the existence of spin-glass state is unreasonable and it is difficult to explain because of the absence of competitive interaction in this sample. In order to clarify this issue, spin kinetic measurements of samples were carried out.

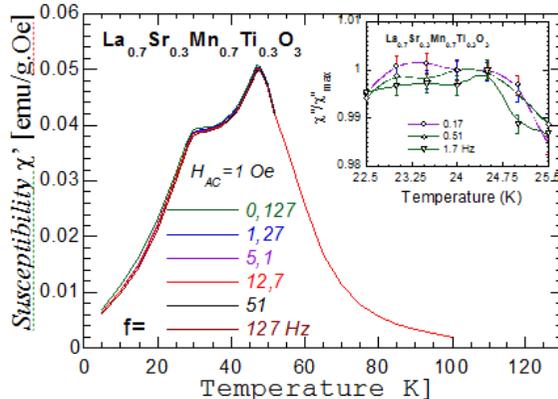


Fig.4. The temperature dependence of AC susceptibility of $La_{0.7}Sr_{0.3}Mn_{0.7}Ti_{0.3}O_3$ sample measured in $H_{AC}=10$ Oe. The insert presents the frequency dependence of the shoulder on the virtual curves.

Figure 4 shows the temperature dependence of the AC magnetic susceptibility of the sample $x = 0.3$ measured in magnetic field $H_{AC} = 1$ Oe with different frequencies. A noticeable point is that all $\chi(T)$ exhibit a peak at $T_C \sim 50$ K and "shoulder" at ~ 25K. The existence of two peaks corresponding to the virtual curves (the inserted figure). However, the absolute value of the magnetic susceptibility depends on the frequency very slightly. Moreover, the peak and the "shoulder" located at ~50K and 25K respectively do not depend on frequencies. These are evidences to believe that the spin-glass state does not exist in the sample in the measured temperature range. In the previous works [15], [23], [24] study on the samples of $La_{0.7}Ca_{0.3}Mn_{1-x}Ti_xO_3$, the authors have suggested that the sample $x = 0.3$ behaves spin glass and ferromagnetic is caused by indirect exchange interaction between Mn^{3+} ion. In the recent study, F.J. Ding et al. also suggests that a spin-glass state could be a result of competing magnetic orders and spin frustration in the sample [25]. However, by the current empirical evidence, we believe that spin configuration of the $La_{0.7}Sr_{0.3}Mn_{0.7}Ti_{0.3}O_3$ sample could be tilt antiferromagnetic (canting). Ferromagnetic could be caused by the incomplete clearing of the spin vector. Anomalies at low temperatures and the difference between the $M_{FC}(T)$ and $M_{ZFC}(T)$ curves in low magnetic field could be merely by hysteresis because of anisotropic.

3.3. The electronic property of $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$.

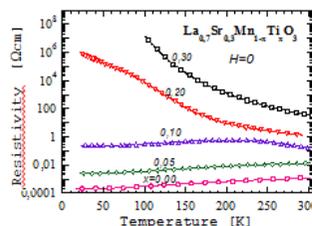


Fig.5. The temperature dependence of resistivity of $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ sample.

Figure 5 describes the temperature dependence of the resistivity of the sample. It is clear that the very rapid increase of the resistivity as increasing the substituted concentration. Moreover, metallic state is not observed in the $x \geq 0.2$ samples even in ferromagnetic phase. There is not any change in form of these curves even around phase transition. We believe that, the substitution Ti^{4+} for Mn^{4+} breaks double exchange interaction and then destroys the hopping of e_g in this interaction, a main factor causing metallic conductivity in this system. As a result, the dielectric (or insulating) regions could be generated at these sites. As the Ti concentration is high enough, the dielectric region / semiconductor becomes border isolates ferromagnetic clusters. Consequently, metallic behavior and the sign of change in resistivity could be no longer even at T_c . This is also observed in the samples of $La_{0.7}Sr_{0.3}Mn_{1-x}Al_xO_3$ [17].

The metallic-insulating transition generated at T_p expected to close to ferro-paramagnetic transition of the samples of $x = 0$ and 0.05 has not been observed because of restriction of measuring system. However, the samples exhibit metallic state in the whole range of measured temperature up to 20K. It is noticeable that the metallic-insulating transition of $x = 0.1$ sample is observed at T_p below T_c (observed in figure 1), there is a "small shoulder" located at T_c as shown in the figure 6.

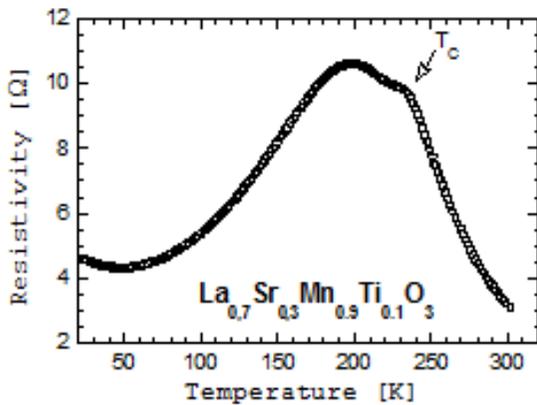


Fig. 6. The temperature dependence of resistivity of $La_{0.7}Sr_{0.3}Mn_{0.9}Ti_{0.1}O_3$

It is similar to the resistive characteristic observed in [26]. The existence of this "small shoulder" could be explained by the hopping of electron e_g in the DE interaction. In the low temperatures, the sample exhibits a conductivity of insulating as observed in some ferromagnetic cobaltite [27]. Such phenomenon is explained by the freezing of ferro-magnetic clusters in the low temperatures. These results also published in [16]. In this study, the sample exhibits a drastic insulator in the range of $T < 50K$. Resistivity is even higher than that of T_p .

The co-existence of a small "shoulder" at $T_c = 235K$ and $T_p = 198K$ suggests that ferro-paramagnetic transition does not directly relate to metal-insulating transitions. In this case, the metal-insulating transition is explained by the competition between metallic-ferromagnetic and insulating-non-ferromagnetic clusters as well as their connection. The "small shoulder" is due to the hopping of conducting electron e_g in the double exchange interaction.

For $x = 0.2$ sample, metallic-insulating transition is not detected, however, the $\rho(T)$ suggests that the formation of the ferromagnetic phase below T_c also affects the conductivity of the sample. The results obtained for the sample $x = 0.2$ by N. Kallel *et al.* [15] shown that the metallic-insulating transition occurs at a temperature of about 125K, far from T_c (about 172K) [15]. The difference between our and Kallel results could be explained by the quality of the sample. The quality of sample particularly phase homogeneous is probably problem causing the differences between the samples in the different studies. Another noteworthy characteristics of the sample x

$= 0.2$ in this study is the coexistence of ferromagnetism and dielectric properties. Dielectric ferromagnetic state is not consistent with the mechanism of DE and it could be explained by the phenomenon of phase separation in the material.

3.4. Influence of Ti substitution on magnetoresistance of the $La_{0.7}Sr_{0.3}Mn_{1-x}Ti_xO_3$ samples.

The magnetoresistance of the samples are examined by isothermal $M(H)$ measurements carried out at different temperatures in the FM-PM transition region. Figure 7 shows the MCE of the samples of $x=0$ and $x=0.05$. For all the ΔH values from 1 T to 6 T, the MCE attained a maximum near ferro-paramagnetic transition temperature with the small ΔH . It shifts toward higher temperature with larger ΔH . This could be explained in term of the double exchange interaction and phase separation phenomenon. The external field orient spin of electron e_g and then the DE interaction could be establish at higher temperature. As applying a high magnetic field, the FM clusters grow greatly in size near T_c . Consequently, the FM-PM transition is quickly broadened with increasing applied field.

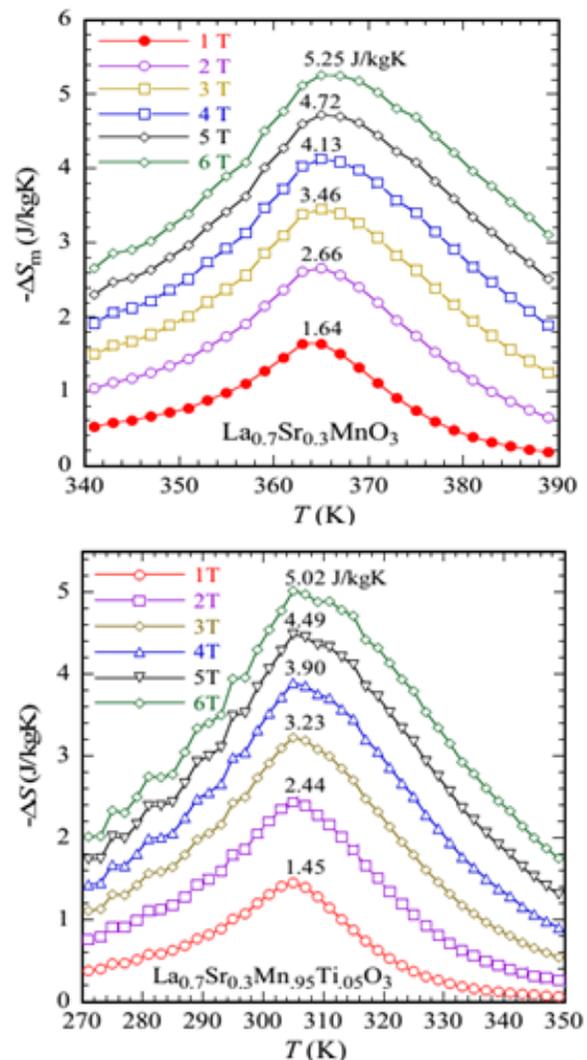


Fig. 7. The temperature dependence of the magnetic entropy changes of the $x=0$ and $x=0.05$ samples in the different changes of applied field.

Entropy change reaches a maximum (with the values indicated in the figures) near the FM-PM transition temperature. The substitution Ti for Mn, as result, shifts the MCE to room temperature and the temperature range existing MCE is broadened.

It can be seen from the figure 7, the substitution Ti decreases $-\Delta S_m$ slightly. However, the relative cooling power $RCP = -\Delta S_m(T, \Delta H) \times \delta_{TFWHM}$ (δ_{TFWHM} is the full width at half maximum of the magnetic entropy change curve), is improved.

IV. Conclusion

The electric, magnetic properties and entropy change of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ compounds have been studied. The replacement a part of Ti^{4+} ion for Mn^{4+} ion reduces the DE interaction couplings between Mn ions. As a result, the magnetism is decreased and system behavior glassy as increasing the Ti content. For fully replacing Ti^{4+} for Mn^{4+} , the canted spin state is formed. The replacement Ti for Mn increases resistivity quickly and the insulating-metallic transition temperature shifts toward lower temperature. The substitution Ti shifts the CME down to room temperature while do not lower the value of entropy change very much. In addition, this effect happened in the wider range of temperature. Moreover, the relative cooling power is improved. These are potentials for the non-gas cooling applications.

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