

# Structure, magnetic and transport properties of Ti-substituted $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$

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## Abstract

Ti-substituted perovskites,  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ , with  $0 \leq x \leq 0.20$ , were investigated by neutron diffraction, magnetization, electric resistivity, and magnetoresistance(MR) measurements. All samples show a rhombohedral structure (space group  $R\bar{3}c$ ) from 10 K to room temperature. At room temperature, the cell parameters  $a$ ,  $c$  and the unit cell volume increase with increasing Ti content. However, at 10 K, the cell parameter  $a$  has a maximum value for  $x = 0.10$ , and decreases for  $x > 0.10$ , while the unit cell volume remains nearly constant for  $x > 0.10$ . The average (Mn,Ti)-O bond length increases up to  $x=0.15$ , and the (Mn,Ti)-O-(Mn,Ti) bond angle decreases with increasing Ti content to its minimum value at  $x=0.15$  at room temperature. Below the Curie temperature  $T_C$ , the resistance exhibits metallic behavior for the  $x \leq 0.05$  samples. A metal(semiconductor) to insulator transition is observed for the  $x \geq 0.10$  samples. A peak in resistivity appears below  $T_C$  for all samples, and shifts to a lower temperature as  $x$  increases. The substitution of Mn by Ti decreases the  $2p-3d$  hybridization between O and Mn ions, reduces the bandwidth  $W$ , and increases the electron-phonon coupling. Therefore, the  $T_C$  shifts to a lower temperature and the resistivity increases with increasing Ti content. A field-induced shift of the resistivity maximum occurs at  $x \leq 0.10$ . The maximum MR effect is about 70% for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ti}_{0.2}\text{O}_3$ . The separation of  $T_C$  and the resistivity maximum temperature  $T_{\rho,max}$  enhances the MR effect in these compounds due to the weak coupling between the magnetic ordering and the resistivity as compared with  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ .

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## I. INTRODUCTION

The  $A_{1-x}A'_x\text{MnO}_3$  perovskites are interesting systems because of the anomalous magnetic and transport properties exhibited by them such as colossal magnetoresistance (CMR), metal-insulator transitions, antiferromagnetic-ferromagnetic ordering, and lattice dynamics associated with phase transitions.<sup>1,2,3,4,5,6,7,8</sup> Zener's double exchange (DE) interaction between  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions through charge carriers in the oxygen  $2p$  orbitals was introduced in order to explain the coupling of magnetic and electronic properties in these compounds.<sup>9,10,11,12</sup> Undoped  $\text{LaMnO}_3$  is an  $A$ -type antiferromagnetic insulator. By substitution of  $\text{La}^{3+}$  with a divalent cation,  $\text{LaMnO}_3$  can be driven into a metallic and ferromagnetic state. Both  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions possess a local spin ( $S=3/2$ ) from their lower  $t_{2g}^3$  orbitals, and  $\text{Mn}^{3+}$  has an extra electron in the  $e_g$  orbital which is responsible for conduction. The spin of the  $e_g^1$  electron in  $\text{Mn}^{3+}$  is ferromagnetically coupled to the local spin of  $t_{2g}^3$  according to Hund's rule. Sr doping induces holes in the  $e_g$  band near the Fermi energy, producing mobile holes and conduction. However, recent studies have shown that DE is not sufficient to explain the complex physics in these compounds, especially as regards the lattice distortions coinciding with the emergence of CMR<sup>13,14</sup>. An understanding of the Sr-doped systems requires one to consider both DE interactions in the  $\text{Mn}^{3+}\text{-O-Mn}^{4+}$  pairs and the strong electron-phonon coupling, including lattice polarons and dynamic Jahn-Teller(J-T) distortions.<sup>15,16</sup> The polaron effect arising from J-T distortion was introduced to explain the electronic transport mechanism in the high temperature region,  $T \approx T_C$ , where a strong electron-phonon interaction is required to reduce the kinetic energy of the conduction electrons. The local J-T distortion of the  $\text{MnO}_6$  octahedron lowers the energy of the  $e_g^1$  electron and the charge carrier can then be localized to form a lattice phonon. Therefore local lattice distortion above  $T_C$  rapidly decreases electron hopping, thus increasing the resistivity.<sup>14</sup> Recently, it was found that polaron hopping was also the dominant conduction mechanism below  $T_C$ .<sup>17,18,19,20</sup> A sharp increase of polaron density at temperatures below  $T_C$  leads to a charge carrier density collapse, which is related to the resistivity peak and the CMR of doped manganites.<sup>21</sup>

In order to understand the unusual magnetic and transport properties of doped perovskites  $A_{1-x}D_x\text{MnO}_3$ , many studies have been carried out by doping the trivalent rare earth site(A site) with divalent atoms(Ca, Sr, Ba, etc).<sup>5,22,23,24,25,26</sup> Other studies have also

shown that substitution for Mn (B site) dramatically affects the magnetic and transport properties of perovskites.<sup>27,28,29</sup> The B site modification has merit in that it directly affects the Mn network by changing the  $\text{Mn}^{3+}/\text{Mn}^{4+}$  ratio and the electron carrier density. Therefore in order to better understand the role of Mn and its local environment in  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ , we studied the effects of replacing some of the Mn with Ti. The structural, magnetic and electrical phase transitions and transport properties of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  with  $0 \leq x \leq 0.20$  have been investigated by neutron diffraction, magnetization, electric resistivity, and magnetoresistance measurements and the results are presented here.

## II. EXPERIMENTAL

Samples of Ti-substituted  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ , with  $0 \leq x \leq 0.2$ , were prepared using the conventional solid state reaction method. Highly purified  $\text{La}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}$  were mixed in stoichiometric ratios, ground, and then pelletized under 10,000 psi pressure to a 1 cm diameter. The pelletized samples were fired at  $1500^\circ\text{C}$  in air for 12 hours, then reground and sintered at  $1250^\circ\text{C}$  for 24 hours in air. X-ray diffraction of the powders was carried out at room temperature using a SCINTAG diffractometer with  $\text{Cu-K}\alpha$  radiation. X-ray diffraction data indicated all samples to be single phase. Powder neutron diffraction experiments were performed at the University of Missouri-Columbia Research Reactor(MURR) using neutrons of wavelength  $\lambda=1.4875 \text{ \AA}$ . The data for each sample were collected between  $2\theta = 5.65 - 105.60^\circ$  at 300K and 10 K. Refinement of the neutron diffraction data was carried out using the FULLPROF program<sup>30</sup>, which permits multiple phase refinements as well as magnetic structure refinements. Magnetic measurements were conducted with a SQUID magnetometer(MPMS, Quantum design). The magnetization curves with zero-field cooling(ZFC) and field cooling(FC) were measured in an applied magnetic field of 50Oe. Resistivity data were obtained using a physical properties measurement system(PPMS, Quantum design) with a standard four-point probe method.

## III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction patterns of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  samples, with  $0 \leq x \leq 0.2$ , at room temperature(RT). All the samples are single phase and all peak

positions can be indexed to  $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_{2.91}$  (JCPDS 50-0308), space group  $R\bar{3}c$ . In order to investigate the details of the structural distortion and the magnetic interactions in these compounds, powder neutron diffraction measurements were performed at different temperatures. Figure 2 shows the neutron diffraction patterns of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  with  $x = 0.0$ ,  $x=0.03$  and  $0.15$  measured at RT and 10 K. All patterns can be fitted with the  $R\bar{3}c$  rhombohedral space group (No. 167) in which the atomic positions are La(Sr): 6a (0,0,1/4), Mn(Ti): 6b (0,0,0); O18e (x,0,1/4). The  $P1$  space group was used to fit the magnetic structure with collinear Mn magnetic moments because of its flexibility. Refined structural and magnetic parameters are listed in Tables I and II for RT and 10K, respectively. For samples with  $x \geq 0.10$ , there is no magnetic ordering at RT since  $T_C < \text{RT}$ , whereas for samples with  $x \leq 0.10$ ,  $T_C > \text{RT}$  magnetic ordering is observed. The arrows on the neutron diffraction patterns of the  $x = 0.0$  sample (Figure 2 ) indicate magnetic reflection peaks that are not present for the  $x = 0.20$  sample at RT. The peak intensities of the magnetic reflections decrease with Ti substitution at both RT and 10 K. In addition, the refinement results confirm that the substituted Ti ions go into B sites, not into A sites, because the ionic radius of  $\text{Ti}^{4+}$  ( $0.605\text{\AA}$ ) lies between the ionic radius of  $\text{Mn}^{4+}$  ( $0.530\text{\AA}$ ) and  $\text{Mn}^{3+}$  ( $0.645\text{\AA}$ )<sup>32</sup>. The tolerance factor, which is the geometric measure of size mismatch of perovskites,

$$t = (r_{(La,Sr)} + r_O) / [(r_{(Mn,Ti)} + r_O)\sqrt{2}] \quad (1)$$

decreases linearly from 0.928 for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  to 0.921 for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{0.8}\text{Ti}_{0.2}\text{O}_3$ , which is in the stable range of the perovskite structure  $0.89 < t < 1.02$ .<sup>26</sup> Therefore, substitution of Mn by Ti does not change the crystal structure itself but changes the bond lengths and the bond angles of the  $\text{MnO}_6$  octahedra.

Fig. 3 plots the lattice parameters  $a, c$  and the unit cell volumes of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  versus the Ti( $\text{Ti}^{4+}$ ) content at room temperature and 10 K. The lattice parameters  $a, c$  and the unit cell volume increase with the Ti content at RT. At 10 K, the lattice parameter  $a$  shows a maximum value at  $x = 0.10$  and then decreases as  $x > 0.10$ , and the unit cell volume increases up to  $x = 0.10$  and becomes almost constant for  $x > 0.10$ . The refined magnetic moment of the Mn atoms indicate that Mn atoms have a high spin state, and the average valence state of the Mn varies from  $3d^{3.5}$  to  $3d^{3.3}$  for  $x=0.0$  and  $x=0.15$ , which suggests that the Ti atoms are in the  $\text{Ti}^{4+}$  state. The values of the temperature factor B of oxygen increase with increasing Ti content which is consistent with the increase of the

Mn-O bond length. This is likely related to the structural disorder in the position of oxygen atoms due to the substitution of Mn for Ti.

The average (Mn,Ti)-O bond length and (Mn,Ti)-O-(Mn,Ti) bond angle extracted from the Rietveld refinement at RT and 10K are shown in Figure 4. The bond length of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  increases up to  $x = 0.15$  and remains constant thereafter for  $x \geq 0.15$ , while the bond angle decreases and attains an anomalous minimum value for  $x = 0.15$  at RT. At 10K, the bond length increases up to  $x = 0.10$  and remains constant for  $x > 0.10$ , while the bond angle decreases with increasing  $x$ . The bond length and the bond angle are closely related to the oxygen positions. Therefore, an increasing (Mn-Ti)-O bond length and a decreasing (Mn,Ti)-O-(Mn,Ti) bond angle are strongly correlated. The changes in bond length and bond angle of  $\text{MnO}_6$  compensate one another to diminish the internal strain induced by  $\text{Ti}^{4+}$ . Since the exchange interaction between Mn-Mn depends on both the bond angle and the bond distance, the decrease in bond angle and the increase in bond length decrease the Mn-Mn exchange interaction which leads to a lower magnetic ordering temperature  $T_C$  (see later discussion of M-T curves).

The electronic bandwidth  $W$  has been used to discuss magnetic and transport properties of perovskites with varied A-site doping.<sup>16,33</sup> The empirical formula of the bandwidth  $W$  for  $\text{ABO}_3$ -type perovskites using the tight binding approximation<sup>24</sup> is

$$W \propto \frac{\cos\omega}{(d_{\text{Mn-O}})^{3.5}}, \quad (2)$$

where  $\omega = \frac{1}{2}(\pi - \langle \text{Mn-O-Mn} \rangle)$  and  $d_{\text{Mn-O}}$  is the Mn-O bond length. The calculated values of  $\cos\omega/(d_{\text{Mn-O}})^{3.5}$  using the refinement results are shown in Figure 4(c). We assumed the bandwidth  $W$  is proportional to the values of  $\cos\omega/(d_{\text{Mn-O}})^{3.5}$ . It is found that the bandwidth  $W$  decreases with increasing Ti content. Further, the bandwidth at RT is smaller than the bandwidth at 10K for a given Ti content. The evolution of the bandwidth follows the change in the  $\langle \text{Mn-O-Mn} \rangle$  bond angle. The decrease in bandwidth reduces the overlap between the O-2p and the Mn-3d orbitals, which in turn decreases the exchange coupling of  $\text{Mn}^{3+}$ - $\text{Mn}^{4+}$ , and the magnetic ordering temperature  $T_C$  as well. For a charge-transfer insulator, the band gap energy  $E_g$  in the insulating phase can be written as  $E_g = \Delta - W$ , where  $\Delta$  is the charge-transfer energy and  $W$  is the O-2p-like bandwidth. In practice,  $\Delta$  changes little in the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  system and thus the bandwidth  $W$  becomes a main factor in tuning the band gap energy.<sup>34</sup> For the  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compounds, the decrease in

bandwidth  $W$  increases the band gap,  $E_g$ , and leads to the metal to insulator transition for  $x > 0.10$ .

Figure 5 shows the magnetization versus temperature (M-T) curves measured under field-cooled (FC) and zero field-cooled (ZFC) conditions in a magnetic field of 50 Oe for the  $x = 0.05, 0.10$ , and  $0.15$  samples. A sharp paramagnetic to ferromagnetic transition is observed at a critical temperature  $T_C$ . Figure 6 shows the Curie temperatures,  $T_C$ , of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  for differing Ti content. The decrease in  $T_C$  is obviously related to the changes in bandwidth as seen in Fig. 4(c). The  $T_C$  drops at a rate of about 10K per Ti.  $\lambda$ -shaped magnetization curves in ZFC emerge for  $x \geq 0.10$  samples. The existence of  $\lambda$ -shaped curves under ZFC may be evidence of the formation of ferromagnetic clusters with a spin glass state. The Ti substitution weakens the exchange interaction and breaks the Mn-O-Mn network, and creates short range ordered ferromagnetic clusters. As more Ti is substituted, more inhomogeneous clusters are formed, which leads to a broadening of the paramagnetic to ferromagnetic phase transition peak. A similar phenomenon has been observed in the  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  system.<sup>26</sup>

Magnetization versus field (M-H) curves of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  at different temperatures are plotted in Figure 7. At 20 K, all samples reach a nearly constant value of magnetization under a field,  $H = 0.6$  T. The estimated magnetic moments of the  $x = 0.0, 0.05, 0.10$  and  $0.15$  samples from magnetization data at 20 K are 3.79, 3.54, 3.24, and  $2.49 \mu_B$  per Mn atom, respectively. These moment values are in good agreement with the neutron diffraction refinement results (see Table II). The theoretically estimated magnetic moments of Mn from its valence state taking into account the dilution effect of  $\text{Ti}^{4+}$ , are 3.70, 3.55, 3.40 and  $3.35 \mu_B$  respectively. This suggests that the decrease of magnetization with increasing Ti content is not only due to the dilution of magnetic  $\text{Mn}^{4+}$  atoms but also due to the weakening of exchange coupling by the cluster formation.

Figure 8 shows the resistivity as a function of temperature under different applied fields for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compounds with  $x = 0.0, 0.05, 0.10$  and  $x=0.15$ . In the temperature range 4 - 300 K, the resistivity of the samples increases as the Ti content increases. The resistivity of  $0.05 \leq x \leq 0.10$  shows a maximum value at temperature  $T_{\rho, \max}$  below  $T_C$ , and then decreases as the temperature decreases. Finally the resistivity increases again as T decreases further for  $x \geq 0.10$ . The difference between  $T_C$  and  $T_{\rho, \max}$  becomes larger as the Ti content increases and  $T_{\rho, \max}$  is lower than  $T_C$ . This behavior is quite different from that

observed in the Ti-substituted  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  series which exhibit large differences between  $T_C$  and  $T_{\rho, \max}$ <sup>25</sup>, and  $T_{\rho, \max}$  is higher than  $T_C$ .<sup>26</sup> For the  $x \leq 0.15$  sample, a metal(semiconductor) to insulator transition (MIT) appears in the low temperature region. The field-induced shift of maximum resistivity to higher temperature appears for the  $x \leq 0.10$  samples, and becomes negligible for  $x \geq 0.15$ . The suppression of the resistivity by the applied magnetic field occurs over the entire temperature range for all samples. At  $T > T_C$ , the suppression of the resistivity becomes weaker. According to the DE mechanism, the mobility of the charge carriers  $e_g$  electrons improves if the localized spins are polarized. The applied field aligns the canted electron spins which should reduce the scattering of itinerant electrons with spins and thus the resistivity is reduced. Therefore an applied magnetic field competes with the thermal fluctuations and maintains magnetic ordering around  $T_C$  for the  $x \leq 0.10$  samples, and thus shifts the  $T_{\rho, \max}$  to higher temperatures.

Figure 9 shows the typical temperature dependence of the magnetoresistance [ $\text{MR} = (\rho_0 - \rho_H)/\rho_0 \times 100$ ] of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  samples with  $0 \leq x \leq 0.20$  under an applied field of 1 and 3T. The maximum magnetoresistance increases with increasing Ti concentration. For example, the maximum MR values are 30%, 55% under 3T for  $x = 0.05, 0.15$ , respectively. The temperature of the MR peak shifts to a lower temperature, approximately 15 K per Ti. It is known that in A-site, electron-doped  $\text{A}_{1-x}\text{A}'_x\text{MnO}_3$  ( $x=0.3$ ) compounds, the metal-insulator transition temperature  $T_{MI}$  coincides with the  $T_c$ , and the metal-insulator transition is strongly coupled with the magnetic ordering transition. Therefore, a strong variation of the electrical resistivity up to several orders of magnitude, namely the colossal magnetoresistance (CMR) effect, occurs upon application of a magnetic field near  $T_C$ . However, for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compounds, the  $T_C$  is different from the metal to insulator transition temperature (MIT). The application of a magnetic field has much more effect on the change of electric resistivity when compared to  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  due to the weak coupling between the MIT and the magnetic ordering. An enhancement of the MR effect is observed in these compounds, similar to that in  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$ <sup>25,26</sup> and  $\text{Pr}_{1-x}(\text{Ca}, \text{Sr})_x\text{MnO}_3$  compounds.<sup>35</sup>

The change of the electronic properties of Ti-substituted  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compounds is strongly related to the electron phonon coupling<sup>14</sup>. Accordingly, in the  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  system, the strong electron-phonon coupling localizes the conduction band electron as a polaron, due to the competition between the self trapping energy  $E_{J,T}$  and



the electron itinerant energy. The electron-phonon coupling constant  $\lambda = E_{J,T}/t$ , where  $t$  is the electron hopping parameter which is proportional to the electronic bandwidth  $W$ . As mentioned above, the substitution of Mn by Ti decreases the overlap of the O-2*p* and Mn-3*d* orbitals due to the decrease in  $W$ , thus increasing the electron-phonon coupling. This results in a shift of  $T_C$  to lower temperatures and an increase of resistivity with increasing Ti content. As a consequence, one should consider a possible dependence of  $E_{J,T}$  on Ti content. We cannot rule out the contribution from  $E_{J,T}$ , even though our data indicate that all the observed  $T_C$  and resistivity changes can be explained, at least qualitatively, by the change in  $W$ . Especially, for  $x \geq 0.15$ , the electron-phonon coupling becomes very strong, and the insulator behavior occurs below  $T_C$  as shown in Figure 8. The changes in bandwidth  $W$  are not large enough to account for the dramatic changes in resistivity, and therefore,  $E_{J,T}$  might be contributing significantly to the change of resistivity in these samples.

It has been proposed that, above  $T_C$ , charge may be localized in the form of J-T polarons.<sup>21</sup> At  $T \geq T_C$ , the resistivity of the CMR materials can be explained by the activated adiabatic polaron equation<sup>36</sup>

$$\rho = AT \exp(E_{hop}/kT) \quad (3)$$

Figure 10 shows the plot of  $\ln(\rho/T)$  as a function of  $1/T$  for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compounds with  $x = 0.00, 0.05, 0.10, 0.15$  and  $0.20$  in the high temperature region with zero field resistivity data. Resistivity of all the samples shows a similar slope at  $T \geq T_C$ , which can be fitted well with the small polaron model indicating the formation of a polaron. The polaron hopping energy  $E_{hop}$  is calculated from the slopes. The calculated values of  $E_{hop}$  are 14.5, 49.8, 132.0, 138.3, and 152.5 *meV* for  $x = 0.00, 0.05, 0.10, 0.15$ , and  $0.20$ , respectively. The increase of  $E_{hop}$  is due to the substitution of Mn by Ti which depletes the oxygen *p* holes and leads to an increase in the polaron binding energy. This further confirms that Ti substitution at Mn enhances the electron-phonon interaction, which decreases  $W$  and increases  $E_{hop}$  at high temperatures. The calculated polaron hopping energy shows a large variation between the  $x = 0.05$  and the  $x \geq 0.10$  samples. This is in good agreement with the sharp increase in resistivity and its temperature dependence. Some studies have also suggested that polaron hopping is the prevalent mechanism to explain resistivity below  $T_C$ .<sup>38,39</sup> However, we were unable to fit the resistivity data of the Ti-doped  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  samples below  $T_C$  with several other polaron models such as the semiconducting model,<sup>40</sup> the variable range

hopping(VHR) polaron model,<sup>41</sup> and the adiabatic polaron hopping model. Only the VHR polaron model works reasonably well for the low temperature region,  $T < 75\text{K}$ , for the insulating state,  $x = 0.10$  sample. There may be other contributions, such as ferromagnetic clusters, which would increase the resistivity of the compound.

#### IV. SUMMARY

The magnetic and electronic transport properties of Ti-substituted  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  have been systematically investigated. All the Ti-substituted  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compositions have a rhombohedral structure, (space group  $R\bar{3}c$ ). The correlation between ferromagnetic  $T_C$  and  $T_{\rho,max}$  becomes weaker and spin glass clusters are expected in the low temperature region with increasing Ti substitution. The resistivity in the high temperature region suggests the formation of localized polarons that affect the strong correlation between local structural changes and the MIT. The decrease of the bandwidth  $W$  decreases the overlap between the O-2*p* and Mn-3*d* orbitals, which in turn decreases the exchange coupling of Mn-Mn and the magnetic ordering temperature  $T_c$  as well. Our studies indicate that Ti substitution at Mn enhances the electron-phonon interaction in these compounds, which decreases the bandwidth and increases the resistivities in the entire temperature range.

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TABLE I: Refined parameters for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compound with  $R\bar{3}c$  space-group at room temperature( $T=300\text{K}$ ). Numbers in parentheses are statistical errors.  $a$  and  $c$  are the lattice parameters.  $m$  is magnetic moment.  $V$  is the unit cell volume.  $B$  is the isotropic temperature parameter.  $\chi^2$  is  $[\text{R}_{wp}/\text{R}_{exp}]^2$  where  $\text{R}_{wp}$  is the residual error of the weighted profile.

| Composition                    | 0.00        | 0.03        | 0.05        | 0.10        | 0.15        | 0.20        |
|--------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| $a$ ( $\text{\AA}$ )           | 5.5038(2)   | 5.5107(1)   | 5.5157(2)   | 5.5225(2)   | 5.5306(2)   | 5.5310(2)   |
| $c$ ( $\text{\AA}$ )           | 13.3553(5)  | 13.3635(4)  | 13.3699(5)  | 13.3845(5)  | 13.4032(6)  | 13.4124(6)  |
| $V$ ( $\text{\AA}^3$ )         | 350.364(18) | 351.445(16) | 352.261(18) | 353.508(21) | 355.042(22) | 355.341(23) |
| $m$ ( $\mu_B$ )                | 2.514(28)   | 2.121(33)   | 1.022(63)   | 0.0         | 0.0         | 0.0         |
| $\chi^2$ (%)                   | 2.81        | 3.28        | 3.60        | 3.23        | 4.64        | 2.98        |
| O, 18e,x                       | 0.5422(2)   | 0.5437(2)   | 0.5448(2)   | 0.5460(2)   | 0.5469(2)   | 0.5461(2)   |
| B( $\text{\AA}^2$ ), La(Sr),6a | 0.882(33)   | 0.8124(33)  | 0.873(35)   | 1.030(42)   | 0.975(43)   | 1.149(40)   |
| B( $\text{\AA}^2$ ), Mn(Ti),6b | 0.423(54)   | 0.556(56)   | 0.574(59)   | 0.364(66)   | 0.394(67)   | 0.404(63)   |
| B( $\text{\AA}^2$ ), O,18e     | 1.221(25)   | 1.248(25)   | 1.306(27)   | 1.501(37)   | 1.475(37)   | 1.586(35)   |

FIG. 1: X-ray diffraction patterns of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  ( $0 \leq x \leq 0.20$ ) at room temperature.

FIG. 3: Lattice parameter  $a$ ,  $c$ , and volume of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  versus Ti content at room temperature and at 10 K.

FIG. 4: Average (Mn,Ti)-O bond lengths(a), (Mn,Ti)-O-(Mn,Ti) bond angles(b) and electronic bandwidth parameter  $\cos\omega/(d_{\text{Mn-O}})^{3.5}$ (c), of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  at room temperature and at 10 K.

FIG. 2: Neutron diffraction patterns of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  ( $x=0.0$ ,  $x=0.03$  and  $x=0.20$ ) at 10 K and RT. (The bottom curves(Yobs-Ycal) are the difference between experimental data and refinement data. The vertical bars indicate the magnetic(bottom) and Bragg(top) peak positions). Arrows indicate some of major magnetic diffraction peaks.

TABLE II: Refined parameters for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compound with  $R\bar{3}c$  space-group at low temperature ( $T=10\text{K}$ ). Numbers in parentheses are statistical errors.  $a$  and  $c$  are the lattice parameters.  $m$  is magnetic moment.  $V$  is the unit cell volume.  $B$  is the isotropic temperature parameter.  $\chi^2$  is  $[\text{R}_{wp}/\text{R}_{exp}]^2$  where  $\text{R}_{wp}$  is the residual error of the weighted profile.

| Composition                    | 0.00        | 0.03        | 0.05        | 0.10        | 0.15        | 0.20        |
|--------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| $a$ ( $\text{\AA}$ )           | 5.4811(1)   | 5.4940(1)   | 5.4989(1)   | 5.5116(1)   | 5.5089(2)   | 5.5053(3)   |
| $c$ ( $\text{\AA}$ )           | 13.2756(3)  | 13.3037(4)  | 13.3137(4)  | 13.3354(4)  | 13.3421(6)  | 13.3746(10) |
| $V$ ( $\text{\AA}^3$ )         | 345.397(13) | 347.756(14) | 348.644(16) | 350.820(15) | 350.652(22) | 351.056(35) |
| $m$ ( $\mu_B$ )                | 3.443(25)   | 3.461(27)   | 3.506(32)   | 3.422(28)   | 3.282(36)   | 2.913(51)   |
| $\chi^2$ (%)                   | 3.23        | 3.51        | 2.89        | 2.69        | 3.72        | 4.90        |
| O, 18e,x                       | 0.5431(1)   | 0.5442(2)   | 0.5448(1)   | 0.5467(1)   | 0.5469(2)   | 0.5472(2)   |
| B( $\text{\AA}^2$ ), La(Sr),6a | 0.167(26)   | 0.240(28)   | 0.302(33)   | 0.318(28)   | 0.449(37)   | 0.269(48)   |
| B( $\text{\AA}^2$ ), Mn(Ti),6b | 0.127(45)   | 0.230(49)   | 0.271(57)   | 0.169(47)   | 0.291(62)   | 0.174(81)   |
| B( $\text{\AA}^2$ ), O,18e     | 0.328(21)   | 0.536(23)   | 0.595(27)   | 0.649(22)   | 0.926(28)   | 0.945(36)   |

FIG. 5: The magnetization versus temperature (M-T) curves of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  ( $x=0.05, 0.10, 0.15$ ) measured under field cooling (FC) and zero field cooling (ZFC) conditions in a magnetic field of 50 Oe .

FIG. 6: The Curie temperature ( $T_C$ ), and the temperature of maximum resistivity ( $T_{\rho,max}$ ) of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compounds with  $0 \leq x \leq 0.20$ .

FIG. 7: Field dependent magnetization of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  ( $0 \leq x \leq 0.20$ ) at different temperatures.

FIG. 8: Electric resistivity  $\rho$  versus temperature for  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  compounds ( $x=0.0$ (a),  $0.05$ (b),  $0.10$ (c), and  $0.15$ (d)) in applied magnetic field  $H=0, 1, 3$ , and  $5$  T. Arrows indicate the  $T_{\rho,max}$ . The inset in (d) is the plot of resistivity of  $x=0.15$  compound (with log scale) in  $H=0$  T.

FIG. 9: Temperature dependence of magnetoresistance of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  ( $0 \leq x \leq 0.20$ ) compounds in the magnetic field of  $H=1, 3$  T.

FIG. 10:  $\ln(\rho/T)$  versus  $1/T$  plots in the high temperature region of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{Mn}_{1-x}\text{Ti}_x\text{O}_3$  ( $0 \leq x \leq 0.20$ ) compounds . Dot line is the fitting line .