Small polarons in $La_{2/3}TiO_{3-\delta}$

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The thermoelectric power and dc conductivity of $La_{2/3}TiO_{3-\delta}$ (δ=0.057, 0.07, and 0.16) were investigated. The thermoelectric power is negative between 80 and 350 K. The measured thermoelectric power of $La_{2/3}TiO_{3-\delta}$ increases linearly with temperature, in agreement with the model proposed by C. Wood and D. Emin [Phys. Rev. B **29**, 4582 (1984)], and represented by $A+BT$. This temperature dependence indicates that the charge carrier in this material is a small polaron. There exists a linear relation between $\log(\sigma T)$ and $1/T$ in the range of 200–300 K, the activation energies for small polaron hopping were 0.15, 0.21, and 0.24 eV for δ=0.16, 0.07, and 0.057, respectively. These properties are discussed in terms of a hopping process involving small polarons. This conclusion is confirmed theoretically. Based upon polaron energies obtained experimentally, several parameters relevant to small polaron transport in this material are estimated. © *2000 American Institute of Physics.* [S0021-8979(00)10117-3]

I. INTRODUCTION

Recently perovskite $RTiO_3$ (R: rare earth element) and its hole doped analog, $R_{1-x}M_xTiO_3$ (M: Ca and Sr), have been proposed as appropriate systems for experimental investigations on the doping-induced insulator–metal transition.[1–9] The end compound $RTiO_3$, where the Ti atom is in the $3d^1$ electron configuration, is a Mott insulator irrespective of the species of the rare earth R. On the other hand, the substitution of the trivalent R ion by the divalent M ion decreases the number of electrons per Ti from 1 (a nominal hole doping), and drives the system metallic.[1–9] A detailed understanding of the nature of these insulator–metal transitions are still lacking, however, and a through experimental and theoretical study of the properties of many different systems is needed to gain further understanding.

As one of the open questions, in this paper, we focus on the problem of carrier localization in the perovskite-type $3d^1$ localized insulator $La_{1-x}Sr_xTiO_3$. An important manifestation of the carrier localization enhancement in the perovskite-type light $3d$ transition metal oxides has been given by Tokura and co-workers.[1,3,7] For small x, the system behaves as a variable range hoppinglike insulator, while for $x_c \sim 0.05$, a metal–insulator transition accompanied by a significant Jahn–Teller effect takes place. In a real system, however, it is very difficult to finely control the band filling without introducing any random potential for electrons. In most cases a hole-doped system remains insulating up to some critical filling level. This may be ascribed to the carrier localization effect arising from the combined effect of the correlation-enhanced effective mass and the random potential, though little is known so far about the detailed nature of such a metal–insulator transition.

As a different approach to these systems, in the present work, we prepared $La_{2/3}TiO_{3-\delta}$ to elucidate the insulating properties of $R_{1-x}M_xTiO_3$. A unique feature of the present system is that both the bandwidth and band filling can be chemically controlled by the degree of oxygen deficiency. $La_{2/3}TiO_{3-\delta}$ was first investigated by Abe and Uchino.[10] Under their experimental conditions, they found that with increasing δ the system changes from an orthorhombic double perovskite to cubic structure via the tetragonal double perovskite.[10,11] With rising oxygen deficiency, the formal valence of titanium is changed from 4+ ($3d^0$) to 3+ ($3d^1$). Also the Ti–O–Ti bond angle increases, which leads to an increase of the one-electron bandwidth of the conduction band.[1–9]

The electronic configurations and magnetic properties of $La_{2/3}TiO_{3-\delta}$ resemble those of electron-doped $MTiO_{3-\delta}$. Electronic doping is known to transform the insulating $MTiO_3$ to a metallic phase, even when the degree of doping is very small.[9,12] However, a similar situation does not arise in the present case.[13,14] Thus, the study of the $La_{2/3}TiO_{3-\delta}$ series can provide important clues to the understanding of the basic electronic properties in Ti-based oxides.

In this report, the thermoelectric power, dc conductivity, and magnetic properties of sintered $La_{2/3}TiO_{3-\delta}$, with a controlled oxygen off-stoichiometry δ, are reported, together with some discussion on the nature of the insulating phase.

II. EXPERIMENT

All samples were prepared by the conventional ceramic method, using dried La_2O_3 and TiO_2 ($3N$) powders as start

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ing materials. The amount of metal in La_2O_3 was determined by quantitative analysis with EDTA. The mixture was preheated at 1073 K in air for 12 h, and then pressed into pellets and sintered at 1723 K for 24 h in an appropriate CO_2, H_2 gas mixture. Thermogravimetric analysis and electron-probe microanalysis (EPMA) were done to estimate the oxygen concentration and cation concentration ratio of the $La_{2/3}TiO_{3-\delta}$ system, respectively. The cation concentration ratio estimated by EPMA nearly agrees with the nominal value. All of the sintered pellets were analyzed, using an x-ray diffractometer with a graphite monochromator and Cu $K\alpha$ radiation with step scanning. Powder diffraction patterns were taken for $60° < 2\Theta < 140°$ with 0.01° step scanning for precise lattice parameter measurements. Silicon powders (5*N*) were used as an internal standard.

The thermoelectric power was measured with a precision digital multimeter in the temperature range of about 80–350 K in a home made device. Both ends of the specimen were placed between two blocks machined from oxygen-free high conductivity copper; a temperature difference of 5–8 K was set up between the two electrodes. Copper–constantan thermocouples were welded to the reverse side of each copper plate to measure both the temperature and the thermoelectric voltage. A Keithley 619 Resistance Bridge, an Advantest TR 6871 digital multimeter, and an Advantest R6161 power supply were used for the conductivity measurement by the four-probe method. dc magnetization measurements were obtained using a superconducting quantum interference device magnetometer (Quantum Design MPMS). Susceptibility–temperature ($\chi - T$) curves were measured under zero-field-cooled condition. The magnetic susceptibility was measured between 4.2 and 300 K at an applied field of 1 T.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the x-ray diffraction pattern of the $La_{2/3}TiO_{3-\delta}$. In addition to lines expected for the fundamental perovskite structure, several superstructure lines can be seen. The unit cell changes from the double orthorhombic perovskite to the pseudo-cubic perovskite configuration, with increasing oxygen deficiency. This change is evidenced by the disappearance of some diffraction peaks, which are characteristic of double perovskites. The profiles of the fundamental 200 lines are shown in Fig. 1(b). As shown in Fig. 1(b): the fundamental (200) line of the $\delta = 0.057$ sample splits into three lines corresponding to (200), (020), and (002). This indicates that the crystals experience an orthorhombic distortion to the double perovskite structure ($Pmmm$).[10,11] With increasing δ in $La_{2/3}TiO_{3-\delta}$ the intensity of superstructure reflection lines gradually decreases. At $\delta = 0.160$, all of the superstructure lines disappeared, as shown in Fig. 1(a). The crystal structure finally changes to the pseudocubic perovskite ($\delta = 0.16$) through the intermediate tetragonal double perovskite ($\delta = 0.07$). From the least-squares fitting method, we obtained the lattice parameters to be $a = 3.876$ Å, $b = 3.886$ Å, and $c = 7.786$ Å for $\delta = 0.057$, $a = b = 3.8980$ Å, $c = 7.774$ for $\delta = 0.07$, and $a = 3.899$ Å for $\delta = 0.16$, respectively.

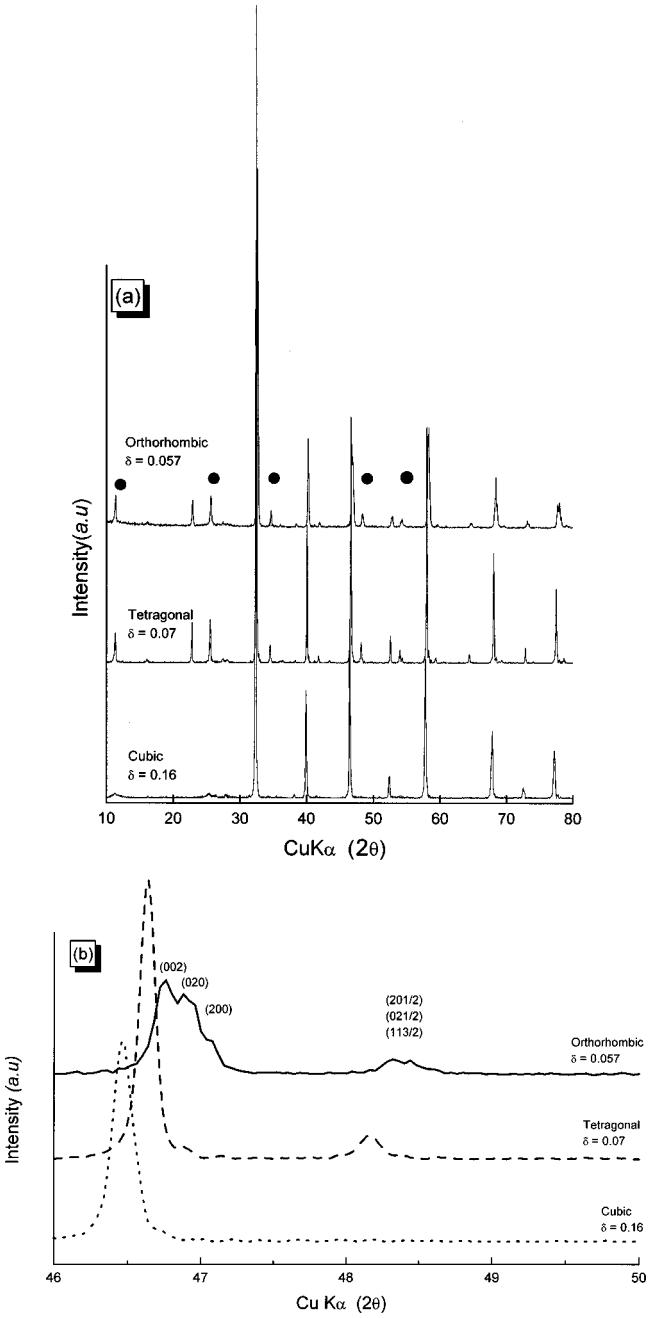

FIG. 1. (a) X-ray diffraction patterns of the $La_{2/3}TiO_{3-\delta}$ system. Closed circles show the superstructure reflection lines originating from the double perovskite structure. (b) X-ray diffraction profile of the 200 line.

The magnetic susceptibility χ measured between 4.2 and 300 K on different samples leads to nearly the same χ values, independent of the oxygen deficiency. The χ curves for $\delta = 0.16$ and 0.057 are reported in Fig. 2. We do not show the magnetic susceptibility data for $\delta = 0.07$ because they are nearly the same as for $\delta = 0.057$. Below 50 K there is sharp upturn which might be due to the presence of a localized electron parameter center. Magnetic susceptibility measurements by Onoda and Yasumoto[5] show that $LaTiO_3$ exhibits canted magnetism. Below ~126 K, an additional magnetic anomaly due to a magnetic transition is also observed. However, the magnetic susceptibility of $La_{2/3}TiO_{3-\delta}$ exhibits a very simple temperature dependence.

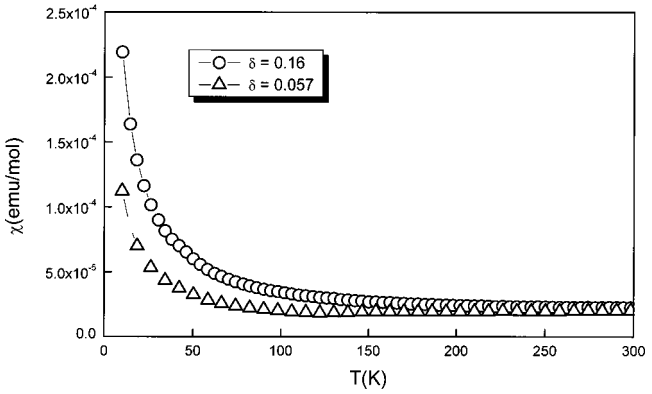

FIG. 2. Magnetic susceptibility vs temperature for $La_{2/3}TiO_{3-\delta}$.

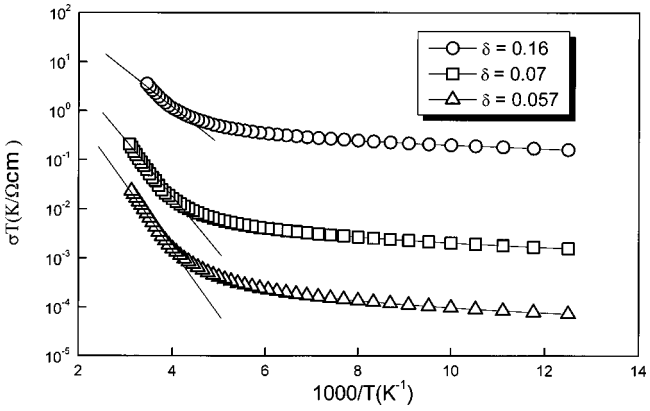

FIG. 4. Arrhenius relation between σT and $1/T$ for $La_{2/3}TiO_{3-\delta}$. The straight lines represent the linear portions in Arrhenius plots.

The thermoelectric power of α of $La_{2/3}TiO_{3-\delta}$ as a function of temperature is shown in Fig. 3. The negative sign of α indicates that $La_{2/3}TiO_{3-\delta}$ is an *n*-type semiconductor over the measured temperature range. We should noted that $La_{2/3}TiO_{3-\delta}$ has a significant concentration of cation vacancies or lattice imperfections. The large random potential fluctuations induce carrier localization, which eventually leads to the formation of small polarons.[13,15,16] The randomness may be due to the La deficiencies and to 3*d* electrons themselves (Ti^{3+}). Thus, the temperature dependence of $La_{2/3}TiO_{3-\delta}$ may be due to the hopping motion of a localized electron on one Ti ion.

The thermoelectric power associated with small polaron hopping in transition metals is generally assumed to depend on the carrier concentration and is given by one of the temperature-independent expressions derived in the high temperature limit.[17,18] However, the measured thermoelectric power of the present material increases linearly with temperature, as shown in Fig. 3. Wood and Emin[19] derived an expression for α for a localized electron system as follows:

$$\alpha = A + BT, \tag{1}$$

where A is the usual entropy contribution to α and B depends on the hopping between inequivalent sites. If the charge carriers are small polarons, the vibration energy term (B term) is important.[19] The values of B determined from a least means squares fit of Eq. (1) to our data are 0.139 $\mu V/K^2$ ($\delta=0.16$), 0.449 $\mu V/K^2$ ($\delta=0.07$), and 0.586 $\mu V/K^2$ ($\delta=0.057$). Here, the value of $B=(k_B^2 z J^2)/(2qE_b^3)$, where z is the number of nearest neighbors, k_B is the Boltzmann constant, q is an electronic charge, J is the intersite transfer energy, and E_b is the small polaron binding energy. From the experimental results, J^2/E_b^3 assumes the values 2.29×10^{13} ($\delta=0.16$), 7.52×10^{13} ($\delta=0.07$), and 9.85×10^{13} ($\delta=0.057$) erg^{-1}.

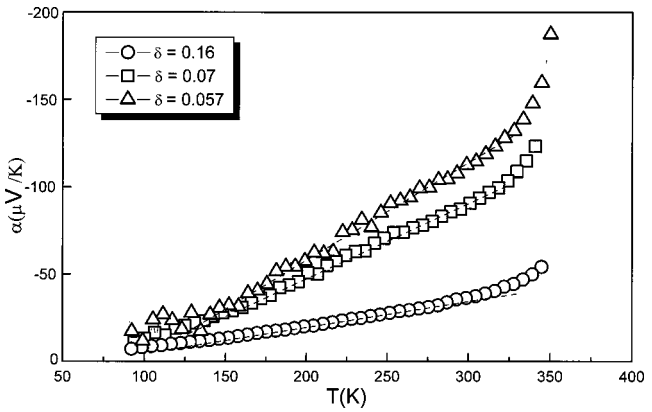

FIG. 3. Thermopower for $La_{2/3}TiO_{3-\delta}$ as a function of temperature. The straight lines are the Emin and Wood relation fitted to data between 150 and 300 K.

Although the experimental results of thermoelectric power measurements suggest a high degree of small polaron hopping, further detailed experimental confirmation is required. If the conductivity data of $La_{2/3}TiO_{3-\delta}$ can be interpreted in terms of a phonon-assisted hopping model, the predicted temperature dependence of the conductivity due to small polaron hopping takes the form[13,14,16,20–22]

$$\sigma T \propto \sigma_0 \exp(-W_H/k_B T), \tag{2}$$

where W_H is hopping energy of small polaron. The Arrhenius relation of σT against $1/T$ in the high temperature range from above 200 to 300 K plotted in Fig. 4 yields good straight lines with hopping energies of 0.15, 0.21, and 0.24 eV for $\delta=0.16$, 0.07, and 0.057, respectively.

Small polaron binding energy was given by $E_b \approx 2W_H$.[23] Then, J can be estimated from the B. Take the hopping energy W_H from the fits to the measured conductivity data (see Fig. 4). From this relation, the values of J are calculated to be 0.35, 1.0, and 1.47 eV for $\delta=0.16$, 0.07, and 0.057, respectively; they decrease with increasing δ.

The decrease in J with increasing δ is expected because the tolerance factor (t) increases as δ increases. The conduction band of this system may be composed of Ti $3d$ t_{2g} and O $2p\pi$ orbitals; its bandwidth is governed by the Ti–O–Ti bond angle.[1–9] Since to our knowledge the Ti–O–Ti bond angle of $La_{2/3}TiO_{3-\delta}$ with a finite value of δ has not been determined, we estimated the changes of tolerance factor t instead of the bond angle. The tolerance factor t describes the relation between the electronic structure and lattice structure. An increase in the tolerance factor facilitates delocalization of charge carriers, enhancing the bandwidth. This means that a decrease in the tolerance factor enhances localization of charge carriers. The cubic perovskite adjusts to a $t<1$ by a

cooperative rotation of the TiO_6 octahedra that buckles the Ti–O–Ti bond angle from 180° to (180°-Θ), where Θ increases with decreasing t so as to lower the space group symmetry from cubic to tetragonal, rhombohedral, or orthorhombic.[24] Thus, with increasing δ the mean separation between Ti atoms increases, and the characteristic transfer energy J decrease. The relative magnitudes of these transfer energies J indicate that the charge carriers are localized in $La_{2/3}TiO_{2.943}$ more deeply than $La_{2/3}TiO_{2.84}$. Then, the strongest electron–phonon interactions must work in $La_{2/3}TiO_{2.943}$ (orthorhombic perovskite) while the electron–phonon interactions working in $La_{2/3}TiO_{2.84}$ (cubic perovskite) must be the weakest ones. A strong electron–phonon interaction induces large displacement of ions, which localizes electrons more deeply and consequently results in a large value for the polaron binding energy.

In order to understand the real feature of a small polaron in $La_{2/3}TiO_{3-\delta}$, it is of interest to estimate several important relevant physical parameters. The value of a small polaron coupling constant, γ_p, which is a measure of the electron–phonon interaction in $La_{2/3}TiO_{3-\delta}$, can be estimated from the relation $\gamma_p = 2W_H/h\nu_{ph}$.[23] Values of γ_p for $La_{2/3}TiO_{3-\delta}$ are found to vary from 7.24 to 12.06. Austin and Mott[23] suggested that a value of $\gamma_p > 4$ usually indicates strong electron–phonon interaction in solids. From the values of γ_p, an estimate of the polaron effective mass, m_p, is obtained, using the relation $m_p = m^* \exp(\gamma_p)$, where m^* is the rigid lattice effective mass. The calculated values of γ_p and m_p/m^* are found to be quite large, indicating strong electron–phonon interaction in these materials, which also supports the formation of a small polaron. Thus, our measurements of the dc conductivity and the thermoelectric power on a variety of oxygen deficient suggests that conduction is subject to the hopping of small polarons between Ti sites.

IV. CONCLUSION

We have studied the transport properties of double perovskite $La_{2/3}TiO_{3-\delta}$ by measurements of electrical conductivity and of thermoelectric power. The measured thermoelectric power of $La_{2/3}TiO_{3-\delta}$ increases linearly with temperature, in agreement with the model proposed by Emin and Wood, as represented by $A+BT$. The electrical conductivity of these materials, which involves electron transfer between Ti^{3+} and Ti^{4+} ions, has been analyzed in the light of a small polaron hopping mechanism. This conclusion is confirmed theoretically. Based upon polaron energies obtained experimentally, several parameters relevant to small polaron transport in this material are estimated.

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