Metal–nonmetal transition in $Ca_3Ti_2O_{7-\delta}$($\delta < 0.003$)

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Electrical condition in transition metal perovskite oxides at low temperatures is a topic of intense current interest. Most of these oxides belong to the class of ABO_3 or its closely linked derivatives. The interest in these materials has arisen because a number of different phenomena (such as super conductivity, metal-insulator transition and GMR) can be seen in these materials [1–4]. Reduced $SrTiO_3$ and $CaTiO_3$ are well-known examples, where the importance of electron doping in a d-orbital of a metallic system has been shown [5]. In this paper we report the electrical conduction properties of the reduced $Ca_3Ti_2O_{7-\delta}$. This compound is a member of the Ruddlesden–Popper type layered compounds with the general formula $Ca_{n+1}Ti_nO_{3n+1}(n = 2)$. Stoichiometric compound $Ca_3Ti_2O_7$ is a good insulator with high resistivity although Ti has a formal valency of 3+. However, the $Ca_3Ti_2O_{7-\delta}$ which shows a metal–nonmetal transition by changing the temperature is the most interesting case [5]. The electrical properties of reduced $Ca_3Ti_2O_{7-\delta}$ have been reported [5], but detailed transport mechanism and properties of charge carrier have not yet been published.

In order to gain insight into the nature of the carrier contributing to transport, we have performed electrical resistivity measurements on electron introduced $Ca_3Ti_2O_{7-\delta}$ over the wide range of temperature. The stoichiometric compound $Ca_3Ti_2O_7$ was synthesized by conventional ceramic method. The starting material, dried $CaCO_3$ and TiO_2 were used. The mixture powder was calcined at 1323 and 1623 K in air with one intermediate grinding. The ground powder was pressed into pellets and fired at 1873 K for 12 hr. The reduced sample was obtained by heating pellets in the flowing hydrogen gas atmosphere. The oxygen concentration in $Ca_3Ti_2O_{7-\delta}$ is that estimated by TGA. The cation concentration ratio estimated by EPMA nearly agrees with the nominal values. δ was obtained to be $\sim$0.003, with experimental errors with $\pm$0.001. The sintered pellets were analyzed, using an X-ray diffractometer with a graphite monochromator and Cu Kα radiation with step scanning. No secondary phases were observed. They can reasonably indexed as a tetragonal ($a = 3.8304$ Å, $c = 19.507$ Å) *I4/mmm*. The electrical resistances were measured as a function of temperature (10–373 K) by a standard four-point technique.

The temperature dependence of electrical resistivity ρ of $Ca_3Ti_2O_{7-\delta}$ is shown in Fig. 1. The $Ca_3Ti_2O_{7-\delta}$ compound shows insulating behavior below 65 K and shows metallic behavior above this temperature, i.e., the ρ–T curve exhibit a peak with metallic behavior above and nonmetallic behavior below this temperature. As can be seen in Fig. 2, above $\sim$150 K the variation of resistivity with temperature is almost linear, but marked deviations from linearity are observed at low temperatures. At high temperatures higher than 150 K, the resistivity follows a linear law [6–8], $\rho = \rho_0 + AT$, with $\rho_0 \sim 70$ mΩ cm and $A \sim 6.4$ mΩ cm/K. A linear temperature dependence of the resistivity data in the metallic phase at high temperature region is well in agreement with reported on $LaNiO_3$ related perovskite oxides and this law has been also observed in high temperature superconductors above T_C [6–8]. Some works have explained such behavior in the frame work of spin polaron formation where the motion is a diffusive process following the Einstein equation [9, 10], i.e., $\sigma = ne^2D/T$, where n is the number of carriers, e is the electron charge and D is the diffusion coefficient. It has been suggested that, in systems in which the current transport is performed by spin polaron [10], the diffusion coefficient is temperature independent, resulting in a linear variation in the resistivity with temperature.

Below 65 K the resistivity shows a nonmetallic behavior with sharp increase, which gives a vanishing conductivity at 0 K. In the above section, we showed T dependence with large coefficient in resistivity of the metallic phases in the reduced $Ca_3Ti_2O_{7-\delta}$ compound. We assumed that the electron–electron interaction (spin polaron) provides the driving force of the metal–nonmetal transition. The electrical transport properties at low temperature (nonmetallic phase) can be explained in terms of either the impurity conduction mechanism or polaron formation. Following the suggestion of Mott, the experimental data were fitted to the expression for the variable range hopping (VRH) mechanism [9, 10]:

$$\sigma = \sigma_0 \exp\left[-\left(\frac{T_0}{T}\right)^{1/4}\right] \tag{1}$$

The constant σ_0 and T_0 in Equation 1 are explained functionally as

$$\sigma_0 = e^2 a^2 \nu_{\mathrm{ph}}\, N(E_{\mathrm{F}}) \tag{2}$$

and

$$T_0 = \lambda\alpha^3/k_{\mathrm{B}}\, N(E_{\mathrm{F}}) \tag{3}$$

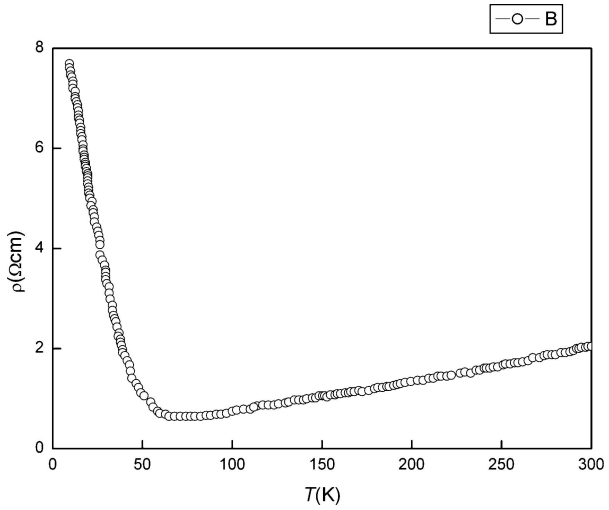

Figure 1 Temperature dependence of electrical resistivity ρ of $Ca_3Ti_2O_{7-\delta}$.

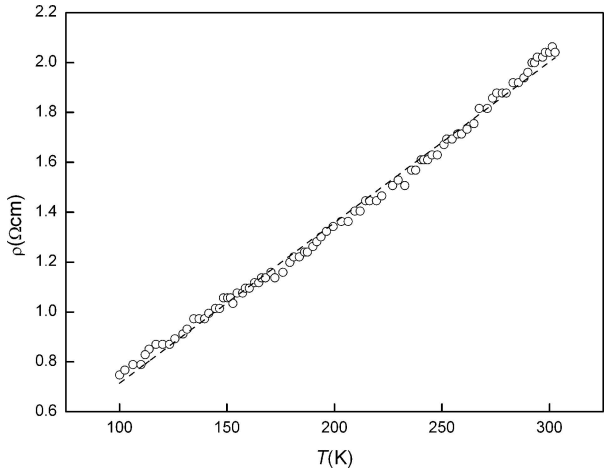

Figure 2 The resistivity of $Ca_3Ti_2O_{7-\delta}$ and the fits to the $\rho = \rho_0 + AT$ law (solid line).

where e is the electron charge, a is the hopping distance, ν_{ph} is a phonon frequency associated with hop (calculated from the Debye temperature, it is around 10^{13} s^{-1}) and $N(E_F)$ is the density of states at the Fermi level. λ ($\approx$18.1) is a dimensionless constant, k_B is Boltzmann's constant and α is inverse rate fall-off the wave function associated with localized states. The hopping distance depends slightly on the temperature following the expression

$$a = \left[\frac{9}{8}\pi\alpha k_B T N(E_F)\right]^{1/4} \quad (4)$$

So the factor σ_0 also depends slightly on the temperature. A logarithmic plot of $\sigma T^{1/2}$ vs. $1/T^{1/4}$ allows an accurate data analysis to be performed. The logarithmic plot of $\sigma T^{1/2}$ vs. $1/T^{1/4}$ and the best fit to Equation 1 for $Ca_3Ti_2O_{7-\delta}$ is shown in Fig. 3. As is observed, the logarithm of $\sigma T^{1/2}$ is linear with $1/T^{1/4}$ in the temperature range between 25 and 70 K approximately, indicating that the conduction mechanism in this material is VRH of the carriers. The slight deviation at low temperatures could be due to impurity conduction [11]

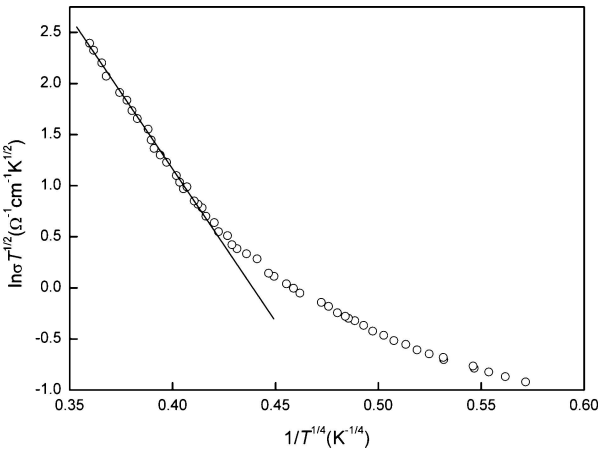

Figure 3 $\sigma T^{1/2}$ vs. $1/T^{1/4}$ for $Ca_3Ti_2O_{7-\delta}$.

or maybe due to the $\sigma_0 \propto T^{-1/4}$ dependence following the percolation theory of hopping for localized electrons with isotropic wave function [7, 8]. The best fit values obtained for $\sigma_0 T^{1/2}$ and T_0 are 12.67 $\Omega^{-1}cm^{-1}$ $K^{1/2}$ and 6.82×10^5 K, respectively. With these results and making use of Equations 2 and 3 the estimated values for $N(E_F)$ and α are 2.8×10^{21} eV^{-1} cm^{-3} and 0.21Å^{-1}.

We have shown that the conduction mechanism at low temperature in nonmetallic phase follows a VRH mechanism, while in the metallic phase the motion is diffusive. A possible explanation is that the carriers in this system could be formed by the coupling of electrons with phonons or magnons, i.e., polarons or spin polarons. The analysis of the low temperature resistivity data leads to reasonable value for the density of states at the Fermi level $N(E_F)$. On the other hand, the polaron's radius ($\sim$22Å at 50 K) obtained for these materials is meaningless for a small polaron. An explanation might be that the Fermi level lies in a narrow impurity band situated in the semiconducting gap for $Ca_3Ti_2O_{7-\delta}$. The impurity conduction is preponderant at low temperatures and is produced by the motion of the carriers between localized states by a VRH mechanism. When temperature is increased, the diminution of semiconducting gap produces a partial overlapping of the valence and conduction bands with impurity band increasing the density of states at the Fermi level.

Acknowledgments

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