Magnetic and transport properties of $Ce_{2/3}TiO_{2.981}$

W H Jung

Department of Electronics, HoWon University 727, Wolha-Ri, Impi, Kunsan, Chŏn Buk, Korea

Abstract. The transport and magnetic properties of A-site-deficient $Ce_{2/3}TiO_{2.981}$ perovskite have been investigated. The electrical conductivity displayed a thermally activated temperature dependence between 200 and 300 K with an activation energy of 0.17 eV. The thermopower measured over a similar temperature range showed little temperature dependence, indicating that transport occurs by means of coupling between localized levels. Analysis of the susceptibility based on the Curie–Weiss law indicated that the Curie constant of the 4f spin of Ce is approximately 40% smaller than that of the free ion due to the crystalline-electric-field effects. Unlike $CeTiO_3$, $Ce_{2/3}TiO_{2.981}$ shows a very simple temperature dependence of its magnetic susceptibility and there is no evidence for the onset of weak ferromagnetism at any temperature. These results are shown to be consistent with transport by means of adiabatic hopping of small polarons.

Recently, there has been tremendous interest in the $3d^1$ system within the study of electron correlations including the metal–insulator transition in a narrow-band system. One of the most extensively investigated compounds is hole-doped $R_{1-x}M_xTiO_3$, where R is a rare-earth element and M is an alkaline-earth ion [1–9].

In particular, Sr substitution at the Ce site ($Ce_{1-x}Sr_xTiO_3$) [5–8] and cation deficiency at the Ce site ($Ce_{1-x}TiO_3$) dope holes into the system [5], and so have been extensively studied in the past. The $Ce_{1-x}Sr_xTiO_3$ system [5–8] is an ideal system to study to determine the influence of band filling on electronic properties, since the end members $SrTiO_3$ and $CeTiO_3$ have d^0 and d^1 configurations, respectively. For small x, the system behaves as a variable-range-hopping-like insulator, while for $x_c \sim 0.04$, a metal–insulator transition accompanied by a significant Jahn–Teller effect takes place. $Ce_{1-x}TiO_3$ systems have been prepared ranging from antiferromagnetic insulating forms and phases that are barely metallic around room temperature (e.g. $CeTiO_3$) to ones from the metallic part of the phase diagram (e.g. $Ce_{0.85}TiO_3$)

The electronic configuration of Ti in $Ce_{2/3}TiO_{2.981}$ is very similar to that for electron-doped $SrTiO_{3-\delta}$. Electron doping is known to transform insulating $SrTiO_3$ readily into a metallic phase, even when the degree of doping is very small [9]. However, a similar situation does not arise in the present case. $SrTiO_{3-\delta}$ belongs to the group of band insulators [9]. There is no report of a band structure of $Ce_{2/3}TiO_{3-\delta}$ to date. However, the band structure of $Ce_{2/3}TiO_{2.981}$ may be considered to resemble the band structure of semiconducting $Ce_{1-x}TiO_3$. Semiconducting $Ce_{1-x}TiO_3$ is a Mott insulator with the gap formed between correlated Ti 3d states of the lower and upper Hubbard band [8].

In this paper, we report on the results on electrical, thermopower, and magnetic properties of $Ce_{2/3}TiO_3$, and data for $CeTiO_3$ are also discussed. The magnetic and

electronic transport properties of this material are compared with those of $Ce_{2/3}TiO_3$. Although the comparison of $CeTiO_3$ with $Ce_{2/3}TiO_3$ is clearly superficial and expectations of similar behaviour would be extremely naive, an investigation of the latter could be intriguing. To our knowledge, in practice, few data have been reported concerning the physical properties of $Ce_{2/3}TiO_3$.

Guaranteed CeO_2 and TiO_2 reagent (Johnson–Matthey, 5N grade) powders were weighed and well ground in an agate mortar. The mixture was preheated at 1073 K in air for 12 h, reground, and reheated at 1273 K for another 12 h. The mixture was pressed into pellets and fired at 1373 K for 48 h in an Al_2O_3 crucible, in a H_2 gas flow. Then the pellets were crushed in an agate mortar, pressed into pellets, and sintered again at 1523 K for 48 h in an Al_2O_3 crucible, in a H_2 gas flow. Thermogravimetric analysis (TGA) and energy-dispersive x-ray microanalysis (EDX) were carried out to estimate the oxygen concentration and cation concentration ratio. The oxygen content of the sample was determined to be 2.981. The composition was found to be nearly identical to the starting composition within the accuracy of 3% of the EDX. The lattice constants were determined by XRD using Si as an internal standard. From the least-squares fitting method, we obtained the lattice parameters $a = 3.856$ Å, $b = 3.8771$ Å, and $c = 7.7520$ Å. The double c-axis length is attributed to the ordered arrangement of Ce ions and vacancies at the A site of perovskite [10, 11].

The dc conductivity of the sample was measured by a standard four-probe technique over the temperature range between 77 K and 300 K. The thermopowers were obtained from measurements made using home-built devices between 100 K and 300 K. Below about 100 K, unfortunately, thermopower is very hard to measure using our home-built device, because of the high resistance. High resistance introduces an open-circuit effect, and makes the noise larger than the signal. Both ends of the specimen were placed between two blocks machined from OFHC (oxygen-free high-conductivity) copper, and a temperature difference of 5–8 K was set up between the two electrodes. Copper–constantan thermocouples were welded onto the reverse side of each copper plate to measure both the temperature and the thermoelectric voltage. The dc magnetic susceptibility was measured over the temperature range between 5 and 300 K, using a SQUID magnetometer (Quantum Design Model MPMS) at applied fields of -1 T to 1 T.

The measurement of the thermopower (α) was carried out to obtain information on the density and sign of the charge carriers. The negative sign of α indicates that $Ce_{2/3}TiO_{2.981}$ is an n-type semiconductor over the temperature range for which the thermopower can be measured (see the inset in figure 1). On the other hand, $CeTiO_3$ has a positive sign of α, indicating hole carriers [5, 6]. It should be noted that the thermopower (α) for $Ce_{2/3}TiO_{2.981}$ is essentially temperature independent over the whole of the temperature ranges employed in this experiment. This result implies that the number of charge carriers does not vary with temperature, and strongly indicates that the charge carriers responsible for the conduction are small polarons. Suppose that one charge carrier ($3d^1$) is created due to oxygen deficiency; one can compare the α-results more quantitatively with Heikes formula modified to exclude spin degeneracy. The general expression for Heikes formula is given as follows [12, 13]:

$$\alpha = \frac{k_B}{e} \ln \left[\frac{2(1-c)}{c} \right] \tag{1}$$

which relates α to the fractional small-polaron concentration c. Equation (1) provides a temperature-independent relationship between the experimentally measured α and the carrier concentration. Application of equation (1) to the highest-temperature α-data from our sample yields the carrier concentration. For this system, it is found to be $c = 0.038$.
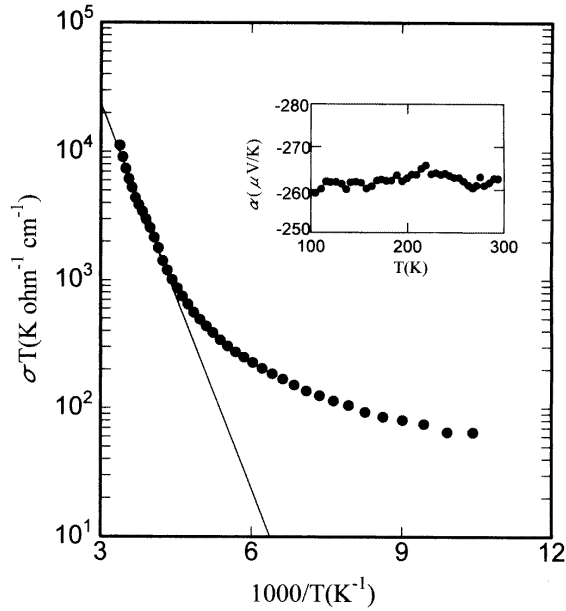
Figure 1. The Arrhenius relation between σT and $1/T$ for Ce$_{2/3}$TiO$_{2.981}$. The inset shows the temperature dependence of the thermopower, α.

The value of c estimated from equation (1) is nearly equal to the Ti^{3+} concentration, which is determined by a thermogravimetric method.

Figure 1 shows the dc conductivity (σT) against $1/T$. Clearly, Ce$_{2/3}$TiO$_{2.981}$ is a semiconductor over this temperature interval. As shown in the inset of figure 1, the temperature independence of α in this material strongly suggests that the charge carriers responsible for the conduction in Ce$_{2/3}$TiO$_{2.981}$ are small polarons. In any case, small-polaron hopping should lead to a temperature-independent α, whose magnitude is primarily dependent on density of the carriers [14, 15]. If the charge carriers responsible for the conduction are small polarons, the temperature dependence of the dc conductivity due to a process of hopping of small polarons predicted theoretically takes the form [15–20]

$$\sigma T^{\gamma} = A_0 \exp\left(\frac{W_{\mathrm{H}} + W_{\mathrm{D}}/2}{k_{\mathrm{B}} T}\right) \tag{2}$$

where W_{H} and W_{D} represent the hopping energy of polarons and the disorder energy.

In equation (2), $\gamma = 1$ for adiabatic small-polaron hopping and $\gamma = 3/2$ in the case of nonadiabatic small-polaron hopping. The conductivity data can be fitted to equation (2) equally well for $\gamma = 1$ and $\gamma = 1.5$. With results from the fit alone, it is difficult to decide whether polaron hopping is adiabatic or nonadiabatic. A check on whether the hopping is adiabatic or nonadiabatic can in principle be made by using Emin and Holstein's conditions [16]. Emin and Holstein give the inequality

$$\hbar \Omega_0 = J^2 \left[\frac{\pi}{4 W_{\mathrm{H}} k_{\mathrm{B}} T}\right] \ll \hbar \omega_0 \tag{3}$$

as the condition for validity of the nonadiabatic limit, where J is the electron-transfer matrix element and ω_0 is the relevant optical-mode lattice fluctuation. In this limit, however, the conductivity is given by the high-temperature form:

$$\sigma = \frac{c(1-c)e^2 J^2}{\hbar k_{\mathrm{B}} T a} \left[\frac{\pi}{4 W_{\mathrm{H}} k_{\mathrm{B}} T}\right]^{1/2} \exp(-W_{\mathrm{H}}/k_{\mathrm{B}} T). \tag{4}$$

For self-consistency, equations (3) and (4) imply that, in the nonadiabatic limit,

$$\Omega_0 = \frac{\sigma a k_B T}{c(1-c)e^2} \exp(W_H/k_B T) \ll \omega_0. \tag{5}$$

Taking a from the lattice spacing (assumed in this discussion as equal to a_c), the carrier concentration c from the thermopower data, and the hopping energy W_H from the fits to the measured dc conductivity data (see figure 1), one obtains the value $\Omega_0 \cong 10^{14}$ Hz. The optical-phonon frequencies for similar transition-metal-based materials lie in the range $\omega_0 = 10^{13}$–10^{14} Hz [21]. This suggests that the nonadiabatic limit, equation (5) is not applicable to that material. Thus, $\gamma = 1$. A least-squares fit based upon equation (2) gives a hopping energy of 0.17 eV. The present experiment cannot separate $W_H + W_D/2$ into individual terms, but $W_D/2$ for crystals is generally less than the experimental error in the determination of W_H [17, 18].
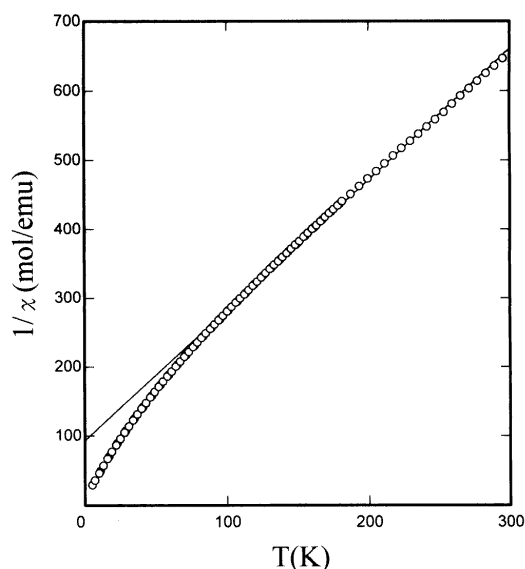

Figure 2. The temperature dependence of the reciprocal susceptibility, $1/\chi$, at 10 mT for $Ce_{2/3}TiO_{2.981}$. The solid line is the Curie–Weiss relation fitted to the data between 150 and 300 K.

Figure 2 shows temperature dependence of the reciprocal magnetic susceptibility measured under a field of 10 mT after cooling the sample to 5 K in the field (1 T). The magnetic susceptibility follows the Curie–Weiss law, i.e., $\chi = C/(T + \Theta)$, over the temperature range from 150 to 300 K. The magnetic susceptibility of the present system is expressed as

$$\chi = \chi_d + \chi_f + \chi_{orb} + \chi_{dia}$$

where the subscripts d and f refer to contributions from the corresponding spins, and where the subscripts *orb* and *dia* are for contributions from Van Vleck orbital paramagnetism and diamagnetism, respectively. Here, the last two contributions are usually temperature independent. The least-mean-squares technique applied to figure 2 yields $C = 0.528$ emu K mol^{-1} and $\Theta = 46$ K. For CeTiO$_3$, the Curie constant was reported to be 0.71 emu K mol^{-1} [5, 6]. Analysis of χ_f based on the Curie–Weiss law indicates that the Curie constant of 4f spins is approximately 40% smaller than that of free ions due to the crystalline-electric-field effect.

Magnetic susceptibility measurements by Onoda and Yasumoto [5, 6] show that CeTiO$_3$ exhibits antiferromagnetism with slight spin canting. Below 60 K, in addition, an additional

magnetic anomaly due to rare-earth ordering is also observed. The small spontaneous magnetization of CeTiO$_3$ at low temperature (below 115 K) is due to the molecular field of the canted moment of the Ti ions acting on the 4f spins of the Ce ions. For Ce$_{2/3}$TiO$_{2.981}$, the deviation from Curie–Weiss behaviour below 150 K may be associated with a weak ferromagnetic moment, although we did not observe any additional magnetic anomalies.
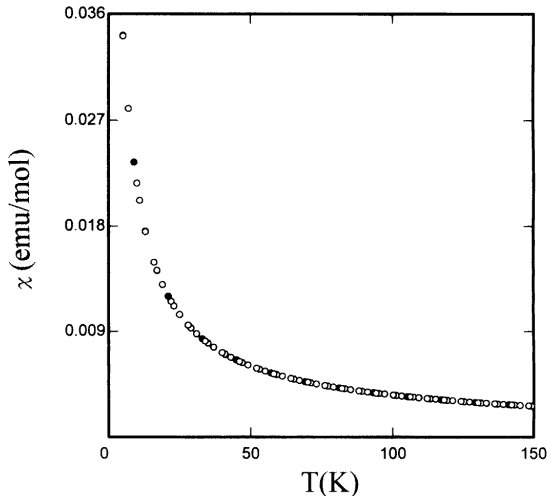

Figure 3. The temperature dependence of the susceptibility for Ce$_{2/3}$TiO$_{2.981}$ measured in a magnetic field of 10 mT after cooling the sample down to 5 K in a field of 1 T (FC: open circles) and in zero field (ZFC: closed circles).

In order to test for possible weak ferromagnetism, zero-field-cooling and field-cooling measurements were conducted, because magnetization depends strongly on magnetic history for ferromagnetic materials. The magnetic susceptibility data for Ce$_{2/3}$TiO$_{2.981}$ are shown in figure 3. The susceptibility values were measured with a field of 10 mT after cooling the sample down to 5 K in a field of 1 T (FC; open circles) or in zero field (ZFC; closed circles). This behaviour is quite different from that usually observed for very weakly ferromagnetic materials [22, 23]. Generally, the magnetic susceptibility is higher in the case of a FC measurement as compared with that for a ZFC measurement, and conversely. However, the magnetic susceptibility of this compound shows a very simple temperature dependence, and there is no evidence for the onset of ferromagnetism at any point. Unlike CeTiO$_3$, Ce$_{2/3}$TiO$_{2.981}$ does not have an obvious canting mechanism.

As the electrical conductivity (see figure 1) and thermopower data (see the inset of figure 1) indicate that the sample is intrinsically semiconducting, with temperature-invariant carrier densities, the magnetic susceptibility of this material is probably due to localized paramagnetic centres associated with the very high concentration of random defects in this crystal. It should be noted that Ce$_{2/3}$TiO$_{2.981}$ has a significant level of cation vacancies or lattice imperfection. This will provide a random-potential effect larger [24] than that in CeTiO$_3$. The random-potential effect may be attributed to carrier localization, which leads eventually to the formation of small polarons [24, 25].

It is generally accepted that the metal–nonmetal transition for hole-doped R$_{1-x}$M$_x$TiO$_3$ is not driven by a decrease of carrier density but by the divergent enhancement of the renormalized electron mass due to electron correlation [26, 27]. A small polaron will be formed if the effective mass of the rigid-lattice carrier (electron and/or hole) is large enough and the coupling to the optical phonons is strong. The electrons (in this case) become trapped in the potential well created by the distortion of the surrounding lattice, and the lattice relaxation will narrow the band even further [25]. As mentioned in the introduction,

$Ce_{2/3}TiO_{2.981}$ has a double perovskite structure; the localization of $3d^1$ electrons is likely to be caused by the quasi-two-dimensionality of the Ti-ion arrangement in the crystal structure. Thus, it is likely that Ti $3d^1$ states with t_{2g} symmetry in $Ce_{2/3}TiO_{2.981}$ will exhibit strong hybridization between oxygen 2p and 3d states due to a large tilting (distortion) of TiO_6 octahedra, resulting in narrow bands and a tendency toward localization [26, 27]. Such localized Ti^{3+} electrons are expected to be accompanied by a Jahn–Teller-type electron–phonon interaction [28] and the consequent formation of small polarons. Therefore, the insulating nature of the $Ce_{2/3}TiO_{2.981}$ system arises from the stability of Ti^{3+} ions as well as from a strong electron–phonon interaction that favours the formation of small polarons.

In summary, measurements of the dc conductivity, magnetic properties, and thermo-power have been made on the perovskite system $Ce_{2/3}TiO_{2.981}$. The thermally activated behaviour of the conductivity together with a virtually temperature-independent thermo-power indicate that the electrical transport occurs by means of hopping between localized levels. The magnitude of the temperature dependence of the conductivity as interpreted from these measurements conforms well with adiabatic small-polaron formation.

Acknowledgment

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