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Electronic carrier mobilities of $BaTiO_3$

H.-I. Yoo*, C.-R. Song[1], D.-K. Lee

School of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea

Abstract

Electronic carrier mobilities of a mixed conductor oxide are one of the most difficult parameters to characterize. A most direct way may be to measure the Hall effect in combination with electronic conductivity, but measurement of the Hall effect in situ at elevated temperatures is never trivial. Thermopower is often employed in association with the conductivity, but the lack of knowledge of the effective densities-of-states and heats-of-transport of the carriers often renders the result unreliable, too. The mobilities of electronic carriers of $BaTiO_3$ thus remain not so well known except for a few estimates of them. Recently, we have evaluated the mobilities of electrons (μ_n) and holes (μ_p) over the temperature range 800–1100 °C by measuring electrical conductivity and chemical diffusivity on undoped and 1.8 m/o Al-doped $BaTiO_3$, respectively, in their mixed n/p regimes. It has been found that for the undoped, $\mu_n = 0.13$ and $\mu_p = 0.08$ cm^2/V-s and for the Al-doped, $\mu_n = 0.08$ and $\mu_p = 1.9910^3\exp(-1.14eV/kT)$ cm^2/V-s over the temperature range examined.

Keywords: $BaTiO_3$ and titanates; Diffusion; Electrical conductivity; Electronic mobility; Perovskites

1. Introduction

Mobilities of electronic carriers, electrons and holes are the basic defect-chemical parameters which are essential to understanding the nature of electronic transport properties of electronic ceramics. The mobility of, say, electrons, is defined as $\mu_n = \sigma_n/ne$ (σ_n the conductivity by carrier electrons; n the electron density; e the elemental charge). In principle, it can thus be determined by measuring n together with σ_n, but while the latter is normally easy to measure, the former is not trivial to determine if not fixed by a known amount of donor impurities. A most common and straightforward way to measure the carrier density may be via the Hall effect,[1–3] but its in situ measurement on mixed conductor oxides at elevated temperatures is normally subjected to nontrivial experimental difficulties such as thermoelectric interferences. Thermopower may also be employed to estimate the carrier density,[4,5] but one should make assumptions on the effective density of states and heat-of-transport of the carrier in question.[5,6] If free electrons are electrically compensated exclusively by oxygen deficit (or metal excess), one may determine n by measuring the oxygen nonstoichiometry via, e.g., thermogravimetry,[7] but one should know the absolute concentration and effective charge of the majority ionic disorder responsible for the nonstoichiometry.

For the system of $BaTiO_3$, thus, limited number of electronic mobility data have been reported.[1,5,7,8] Largely based on the Hall mobility data on n-type $BaTiO_3$ of single crystal up to 1000 K by Seuter,[1] Ihrig[9] proposed a (non-adiabatic small polaron) hopping mobility, $\mu_n \propto T^{-3/2}\exp(-0.021eV/kT)$ above the Curie temperature (ca. 400 K). For p-type $BaTiO_3$, however, the situation is much worse: to the best of the authors' knowledge only one datum of Hall mobility is reported by Seuter,[1] that is $\mu_p = 0.02$ cm^2/V-s at 700 K for single crystal of undoped $BaTiO_3$. Later in their defect chemical analysis of the electrical conductivity of undoped $BaTiO_3$, Chan et al.[10] first quoted Ihrig[9] for the electron mobility as

$$\mu_n = 8080T^{-3/2}e^{-0.021\mathrm{eV/kT}}\,\mathrm{cm^2/Vs} \quad (1)$$

and on the basis of the p-type conductivity variation vs oxygen activity, reasoned that $\mu_n > \mu_p > \mu_n/3$ to propose

$$\mu_p = \mu_n/2 \quad (2)$$

as a reasonable estimate for all temperatures. These mobilities have since been rather widely employed in defect chemical analyses of electrical properties of $BaTiO_3$.[11,12] Eq. (1) indeed seems to be a reasonable

* Corresponding author. Tel.: +82-2-880-7163; fax: +82-2-884-1413.
E-mail address: hiyoo@plaza.snu.ac.kr (H.-I. Yoo).
[1] Now with Hynix Semiconductor Inc., Korea.

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estimate: For undoped $BaTiO_3$, thermopower in association with conductivity has yielded a value $\mu_n = 0.16$ cm^2/Vs in the temperature range 1000–1200 °C,[5] while Eq. (1) gives $\mu_n = 0.15$–0.12 cm^2/Vs over the same temperature range. But, the validity of Eq. (2) has not ever been tested.

In this work, we determine the both mobilities on undoped polycrystalline and 1.8 m/o Al-doped single crystal $BaTiO_3$, respectively, by using the total electrical conductivities and chemical diffusivities in their n/p mixed regimes at elevated temperatures. It is emphasized that in this approach, there is no need to have recourse to any ad hoc assumptions regarding e.g., the densities of states.

2. Theoretical background

The equilibrium defect structure of undoped or acceptor-doped $BaTiO_3$ is schematically as shown in Fig. 1:[11,13] the majority type of disorder $[V_O^{\bullet\bullet}] \approx [A']/2$, where A′ denoting the intentionally doped or background acceptor impurities or intrinsic acceptors ($V''_{Ba}$and/or V''''_{Ti}), reigns an extended range of oxygen activity downward from $a_{O_2} = 1$. In this n/p mixed regime, the total conductivity of $BaTiO_3$ is given as[13]

$$\sigma = \sigma_{ion} + \frac{1}{2}\sigma_{el,m}\left[\left(\frac{a_{O_2}}{a^*_{O_2}}\right)^{1/4} + \left(\frac{a_{O_2}}{a^*_{O_2}}\right)^{-1/4}\right] \quad (3)$$

where σ_{ion} stands for a constant, ionic conductivity. The minimum electronic conductivity, $\sigma_{el,m}$, that falls at a specific oxygen activity $a^*_{O_2}$, conveys the information on the mobility product or [13]

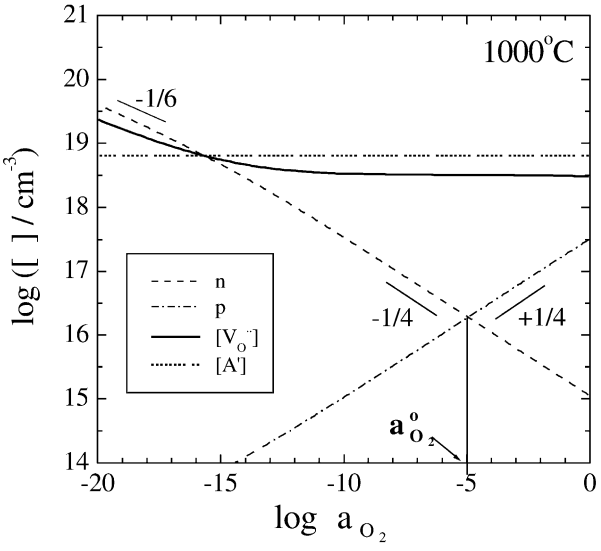

Fig. 1. Defect concentrations vs. oxygen activity of undoped $BaTiO_3$ at 1000 °C. For the numerical values used in calculation, see the Ref. 17.

$$\sigma_{el,m} = 2K_i^{1/2} e(\mu_n \mu_p)^{1/2} \quad (4)$$

where $K_i(=np)$ is the intrinsic electronic excitation equilibrium constant. Furthermore, it can be shown that the oxygen activity $a^*_{O_2}$ is related to another specific activity $a^o_{O_2}$at which n≡p (see Fig. 1) as

$$a^*_{O_2} = a^o_{O_2}(\mu_n/\mu_p)^2 \quad (5)$$

Once K_i, $\sigma_{el,m}$, $a^*_{O_2}$, and $a^o_{O_2}$ are known, one can, thus, evaluate each mobility via Eqs. 4 and 5.

As seen in Eq. (3), $\sigma_{el,m}$ and $a^*_{O_2}$ along with σ_{ion} can be easily determined from a total conductivity isotherm. The rest, K_i and $a^o_{O_2}$ can be obtained either from a nonstoichiometry isotherm,[14] or from a chemical diffusivity isotherm[13]

$$\tilde{D} = \tilde{D}^o t_{el}/\cosh\ln\left(a_{O_2}/a^o_{O_2}\right)^{1/4};$$
$$\tilde{D}^o \equiv kT\sigma_{ion}/2e^2K_i^{1/2} \quad (6)$$

with the aid of σ_{ion} as determined from Eq. (3), where t_{el} stands for the electronic transference number that is again evaluated from the total conductivity via Eq. (3). Therefore, by measuring the isotherms of conductivity and chemical diffusivity, one can determine the electronic mobilities.

3. Experimental

The total conductivity and chemical diffusivity were measured as functions of oxygen activity in the n/p mixed regime (ca.$-18 \leqslant \log a_{O_2} \leqslant 0$) at different temperatures of 800–1100 °C by a dc 4-probe and conductivity relaxation technique, respectively, on undoped polycrystalline $BaTiO_3$ (99.995% purity with a 94±1% sintering density and 43±8 μm grain size) and 1.8 m/o Al-doped single crystal $BaTiO_3$, respectively. For experimental details, the reader is referred to Refs. [15] and [16].

4. Results and discussions

Figs. 2 and 3 show the typical isotherms, e.g., at 1000 °C, of total conductivity and chemical diffusivity of both the undoped and Al-doped $BaTiO_3$, respectively. The solid lines are the best fitted ones to Eqs. 3 and 6, respectively. From the conductivity isotherms at different temperatures, one evaluates via Eq. (3) the three parameters, σ_{ion}, $\sigma_{el,m}$ and $a^*_{O_2}$, which are respectively shown in Fig. 4. From the diffusivity isotherms, $\tilde{D}^o$ and $a^o_{O_2}$ are obtained, via Eq. (6), as shown in Fig. 5. The former in association with σ_{ion} (in Fig. 4), in turn, yields K_i values via Eq. (6). The results are shown in

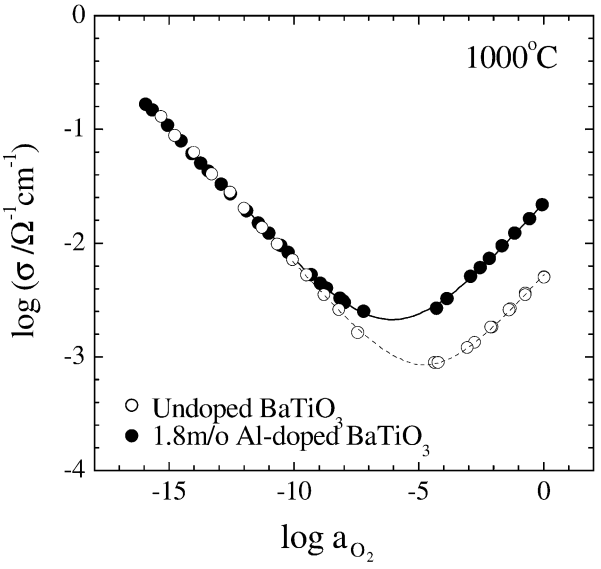

Fig. 2. Electrical conductivity isotherms of undoped polycrystalline (○) and 1.8 m/o Al-doped single crystal (●) $BaTiO_3$ at 1000 °C. The solid and dashed lines are the best-fitted to Eq. (3) in the text, respectively.

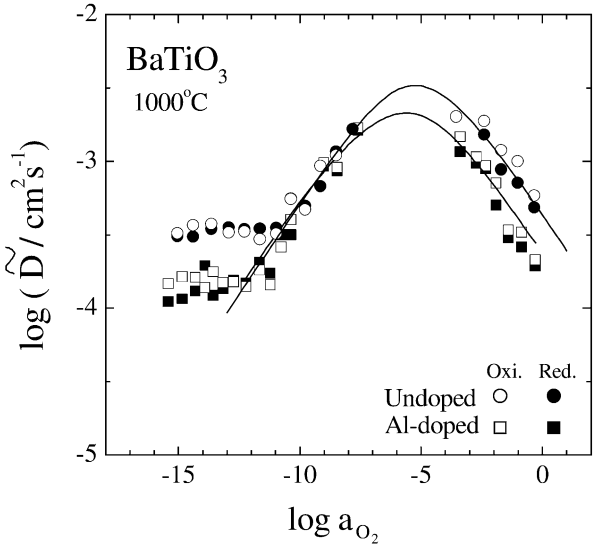

Fig. 3. Chemical diffusivity isotherms for undoped polycrystalline $BaTiO_3$ (○,●) and 1.8 m/o Al-doped $BaTiO_3$ single crystal (□, ■) at 1000 °C, respectively. Solid lines are the best-fitted to Eq. (6) in the text.

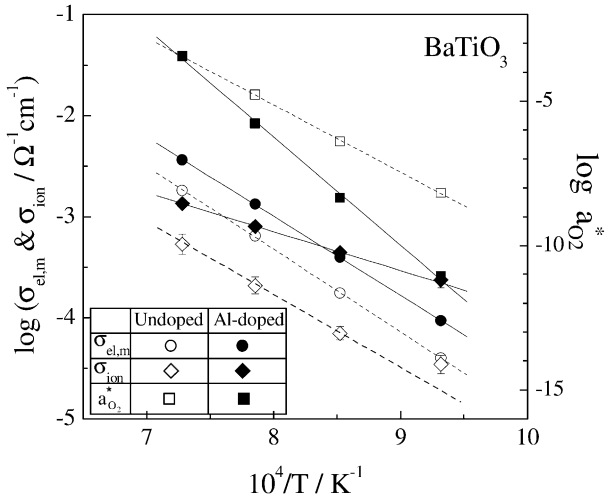

Fig. 4. Variation of log $\sigma_{el,m}$, log σ_{ion} and log $a^*_{O_2}$ as extracted from Fig. 2 vs. reciprocal temperature for undoped polycrystalline (open symbols) and 1.8 m/o Al-doped single crystal (solid symbols) $BaTiO_3$.

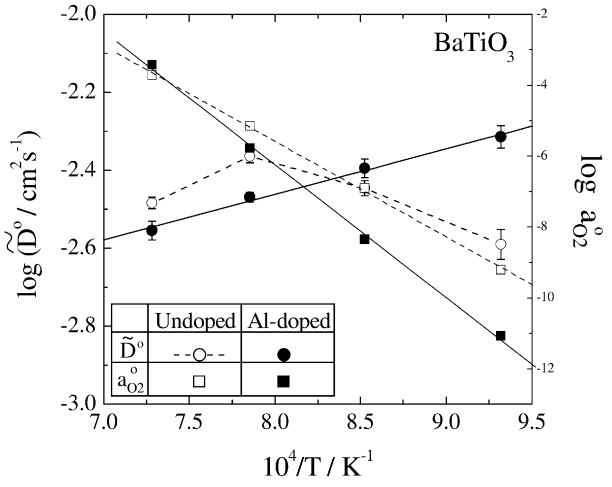

Fig. 5. Log $\tilde{D}^o$ and log $a^*_{O_2}$ vs. reciprocal temperature for undoped and 1.8 m/o Al-doped $BaTiO_3$, respectively.

Fig. 6. It is noted that the slopes correspond to the thermal band gaps: 3.2 eV for the undoped and 2.2 eV for the 1.8 m/o Al-doped. The difference appears to be unusually large, but its origin is not immediately clear.[16] Nevertheless, it is emphasized that K_i has been evaluated only from the experimental data of conductivity and diffusivity without using any assumptions on the densities of states as has been practiced in literature.[5]

Finally, the electronic mobilities are separately determined via Eqs. (4) and (5) as shown in Fig. 7, where they are compared with the values expected from Eqs. (2) and (3). For the undoped case, the present values may be favorably compared with the expected ones for both electrons and holes, but for the Al-doped case, the present values are 3–5 times smaller for electrons and differ even in their dependence on temperature for holes.

As is seen, the both mobilities for the undoped $BaTiO_3$ are fairly insensitive to temperature and hence, may be best estimated at $T > 800$ °C (for the reasons discussed in Refs. [13] and [17]) as

$$\mu_n = 0.13 \pm 0.02 \text{ cm}^2/\text{Vs}; \quad \mu_p = 0.081 \pm 0.017 \text{ cm}^2/\text{Vs}. \tag{7}$$

For the 1.8 m/o Al-doped $BaTiO_3$, on the other hand, the hole mobility appears to be thermally activated while the electron mobility is temperature-insensitive or

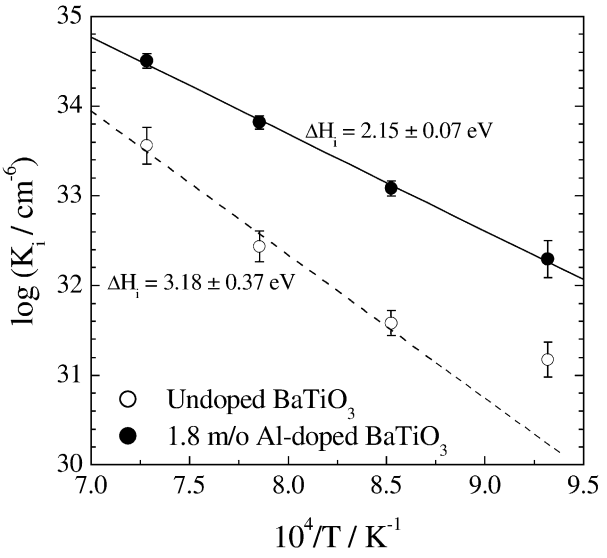

Fig. 6. log K_i vs. reciprocal temperature for undoped and 1.8m/o Al-doped $BaTiO_3$, respectively. The dashed lines are the best-fitted (with the datum at 800 °C rejected for K_i).

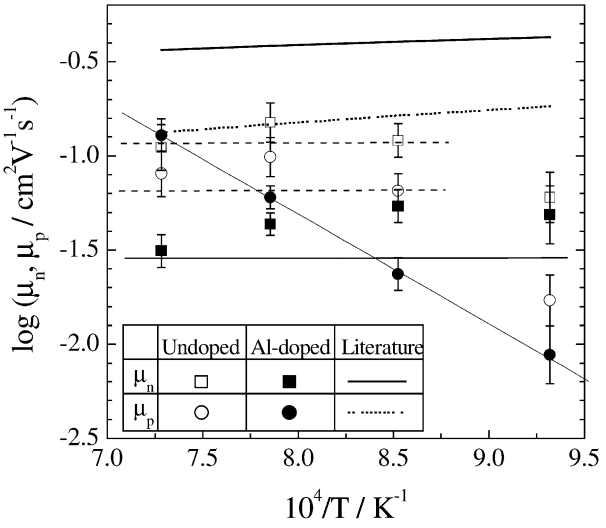

Fig. 7. Mobilities of electrons and holes, μ_n and μ_p vs. reciprocal temperature for undoped and 1.8 m/o Al-doped $BaTiO_3$, respectively.

$$\mu_n = 0.044\pm0.010\ \mathrm{cm^2/Vs};$$

$$\mu_p = \left(1.99^{+0.39}_{-0.32}\right) \times 10^3 \exp[(-1.14\pm0.02)\mathrm{eV/kT}]\mathrm{cm^2/Vs} \quad (8)$$

in the entire temperature range examined. These mobility behaviors suggest that electron and hole conduction are band-like for the undoped $BaTiO_3$. For the 1.8 m/o Al-doped $BaTiO_3$, on the other hand, while electron conduction remains band-like, hole conduction is small-polaron-like. It is supported by the magnitudes of the heats-of-transport of electrons and holes as determined from the thermopower:[6] for the undoped case, they are respectively on the order of thermal energy kT and for the Al-doped, while the heat of transport of electron remains on the order of kT, that of holes is 0.9 eV, close to their hopping energy. Nevertheless, the physico-chemical origin of the hopping energy of 1.1 eV is yet to be elucidated.

5. Conclusion

The electronic carrier mobilities of $BaTiO_3$ could be determined from the total conductivity and chemical diffusivity isotherms in its n/p mixed regime. They are best estimated at elevated temperatures (>800 °C) as $\mu_n = 0.13\pm0.02$ cm^2/Vs; $\mu_p = 0.081\pm0.017$ cm^2/Vs for the undoped system and $\mu_n = 0.044\pm0.010$ cm^2/Vs; $\mu_p = \left(1.99^{+0.39}_{-0.32}\right) \times 10^3 \exp[(-1.14\pm0.02)\mathrm{eV/kT}]\mathrm{cm^2/Vs}$ for the 1.8 m/o Al-doped, suggesting a polaron-like conduction of holes in Al-doped $BaTiO_3$ while a band-like conduction for the rest. We thus conclude that $\mu_n = 8080T^{-3/2}e^{-0.021\mathrm{eV/kT}}\mathrm{cm^2/Vs}$ [Eq. (1)] may be a good estimate for the mobility of electrons within an order of magnitude, but the hole mobility, $\mu_p = \mu_n/2$ [Eq. (2)] should be applied with care particularly for acceptor-doped case.

Acknowledgements

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