



P-Type Partial Conductivity of Donor(La)-Doped BaTiO₃

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Abstract. *P*-type partial conductivity has been determined on donor (La_{Ba}[•])-doped BaTiO₃ in full thermodynamic equilibrium state at a fixed temperature of 1200°C: For the nominal compositions of Ba_{0.99}La_{0.01}Ti_{0.9975}O₃, Ba_{0.99}La_{0.01}TiO₃ and Ba_{0.985}La_{0.01}TiO₃, the *p*-type conductivity is found to vary with oxygen activity as $\sigma_p = (\sigma_m/2)(a_{O_2}/a_{O_2}^*)^{+1/4}$ with $\sigma_m \approx 0.01 \text{ S cm}^{-1}$ and $a_{O_2}^* \approx 32, 120, 310$, respectively, in the a_{O_2} region where conventionally the electronic conductivity varies as $\sigma \propto a_{O_2}^{-1/4}$ and hence, the doped donors are believed to be compensated by cation vacancies (say, $[\text{La}_{\text{Ba}}^{\bullet}] \approx 4[V_{\text{Ti}}''']$). This experimental fact supports that in the vicinity of the stoichiometric composition of the system which falls approximately at $a_{O_2} = a_{O_2}^*$, while cation vacancy concentration is fixed by the donor concentration, oxygen vacancy concentration in the minority is also essentially fixed, thus, keeping the activity of TiO₂ (or BaO) fixed. It is consequently suggested that donor-doped BaTiO₃ contains a second phase even in its stoichiometric regime.

Keywords: MLCC, donor-doped BaTiO₃, *p*-type conductivity, thermopower, defect structure

1. Introduction

BaTiO₃ is one of the essential substances of modern electroceramics, e.g., multi-layer ceramic capacitors (MLCC), positive-temperature-coefficient resistors (PTCR), ferroelectric random access memories (FRAM), etc. Furthermore, as a mixed ionic electronic conductor, it serves as a prototype of perovskite oxides which are now finding a variety of electrochemical applications, e.g. solid oxide fuel cells, batteries, sensors, electrochromics, etc.

As nearly all of its important properties as well as its processing are defect-structure-sensitive, its defect structure has long been a subject of intensive and extensive studies [1]. The defect structure is rather well understood particularly for acceptor-doped and undoped cases despite an ambiguity with the identity of acceptor species for the latter [2, 3]. For the case of donor-doped BaTiO₃, on the other hand, there still remain controversies concerning the majority disorder types depending on the thermodynamic variables [4, 5]. Nevertheless,

it seems to be accepted that as shown in the Kroger-Vink diagram in Fig. 1, the majority disorder types are electrons (e[']) and oxygen vacancies (V_O[•]); electrons and doped donors (say, La_{Ba}[•]); the donors and Ti vacancies (V_{Ti}^{'''}) [5, 6] with increasing oxygen activity a_{O_2} (=P_{O₂}/atm) over an experimentally viable range of, say, 10⁻¹⁸ to 1 at elevated temperatures. This sequence has been basically deduced from the electrical conductivity variation with a_{O_2} : the electrical conductivity, that is essentially due to electrons for donor doped BaTiO₃, varies apparently as $\sigma \propto a_{O_2}^{-m}$ with $m \approx 1/6, 0$ and $1/4$ with increasing a_{O_2} .

If the defect structure of Fig. 1 is correct, then in the middle of the disorder regime of La_{Ba}[•] and V_{Ti}^{'''} where $m \approx 1/4$ should fall the electronic stoichiometric composition where electron concentration is exactly equal to that of holes (i.e., $n \equiv p$) and hence, a *p*-type conductivity would have to be seen because the latter is to vary opposite to the electron conductivity. Up to date, however, the *p*-type conductivity has not been reported on donor-doped BaTiO₃.

We have recently determined the *p*-type conductivity on donor(La_{Ba}[•])-doped BaTiO₃ in fully equilibrated state and evaluated therefrom the hole transference

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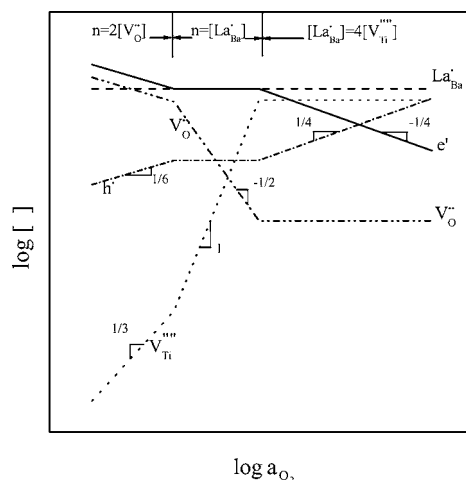


Fig. 1. Kroger-Vink diagram of donor (La_{Ba}^*)-doped BaTiO_3 .

number against the oxygen activity a_{O_2} ($\equiv P_{\text{O}_2}/\text{atm}$). We hereby report the result and discuss its implications.

2. Experimental

We prepared three kinds of specimens with nominal compositions $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\text{O}_3$ (designated as V_{Ti}), $\text{Ba}_{1-3x/2}\text{La}_x\text{TiO}_3$ (as V_{Ba}) and $\text{Ba}_{1-x}\text{La}_x\text{TiO}_3$ (as E) all with $x = 0.01$ originally for the purpose of sorting out the type of defect among the three possibilities $\text{V}_{\text{Ti}}^'''$, $\text{V}_{\text{Ba}}^''$ and e' that can compensate the impurity donors La_{Ba}^* in air atmosphere. The batch powders were synthesized into the three different compositions by a Pechini method [7, 8], calcined at 900°C in air for 3 hours, formed into disks under a uniaxial pressure of 24 MPa, followed by isostatic cold pressing under 200 MPa, and finally sintered at 1400°C in air for 6 hours. The sintered disks were of ca. 91% bulk density with grain sizes of no larger than $1 \mu\text{m}$.

The sintered disks were cut into parallelepipeds measuring $1.8 \times 2.4 \times 15.1 \text{ mm}^3$ and Pt-electrodes were appropriately attached to measure the conductivity by a four-probe d.c. technique and the thermopower by heat pulse as well as steady state techniques. For experimental details, the reader is referred to Ref. [9].

The conductance and thermopower were simultaneously measured *in situ* as functions of oxygen partial pressure in the range of 1 atm down to 10^{-15} atm at a fixed temperature 1200°C . The conductivity was subsequently evaluated from the as-measured conductance simply by taking into account the geometric factor of the specimen without correcting against ca. 9% poros-

ity of the specimens. The oxygen partial pressure was controlled by N_2/O_2 and CO/CO_2 mixtures and monitored by a zirconia-based electrochemical cell.

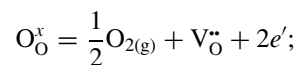
It is notorious that re-equilibration kinetics of donor-doped BaTiO_3 is extremely sluggish compared to undoped or acceptor-doped counterparts [10, 11]. Re-equilibration kinetics was, thus, closely monitored by observing conductivity relaxation upon a change of oxygen activities in order to ensure complete thermodynamic equilibrium of the specimens with their surrounding atmosphere. The kinetics was indeed much more sluggish in general and in a particular oxygen activity region, even prohibitively sluggish. For instance, it took 30–40 min, 20–40 hr, and 4–6 hr for complete re-equilibration upon oxygen activity changes from $\log a_{\text{O}_2} = 0.0$ to -0.61 , from -4.4 to -6.3 and from -12.5 to -13.3 , respectively, at 1200°C . Consequently, measurement had to be limited to a particular temperature 1200°C . Furthermore, re-equilibration was considered to be impractical time-wise in the oxygen activity range of $-12 < \log a_{\text{O}_2} < -8$, and hence, data were missing there. This kinetic aspect will be the subject of a forthcoming publication.

3. Results and Discussions

The conductivity and thermopower isotherms at 1200°C are as shown in Fig. 2 for the three different specimens. As is seen, the conductivity, σ , apparently varies as

$$\sigma \propto a_{\text{O}_2}^{-m} \quad (1)$$

with the values for the oxygen exponent $m \approx 1/4, 0$ and $1/6$ in turn with decreasing oxygen activity from 1. This behavior has been repeatedly observed earlier [12, 13] and explained, if, e.g., $\text{V}_{\text{Ti}}^'''$ is in the majority as recently claimed [5, 6], in terms of the defect chemical scheme:



$$[\text{V}_\text{O}^*]n^2 = K_R a_{\text{O}_2}^{-1/2} \quad (2)$$



$$[\text{V}_\text{Ti}^'''][\text{V}_\text{O}^*]^2 = K_T a_{\text{TiO}_2}^{-1} \quad (3)$$

$$0 = e' + h^*; \quad np = K_i \quad (4)$$

$$[\text{La}_{\text{Ba}}^*] + 2[\text{V}_\text{O}^*] + p = 4[\text{V}_\text{Ti}^'''] + n \quad (5)$$

where [] denote the concentration of the structure element therein, $n \equiv [e']$, $p \equiv [h^*]$, a_k the activity of

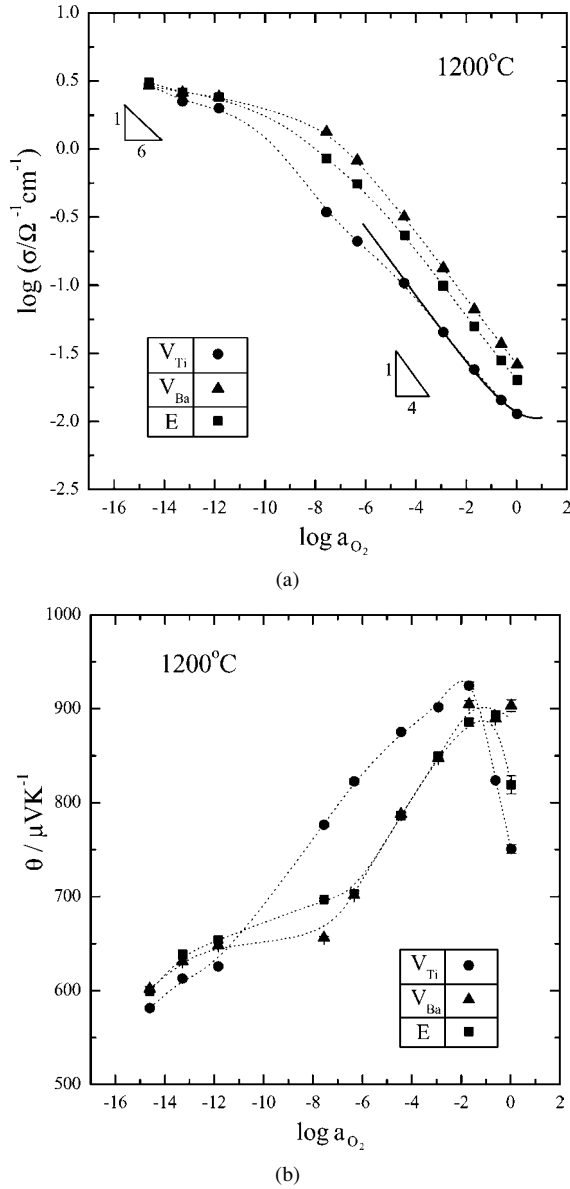


Fig. 2. Electrical conductivity (a) and thermoelectric power (b) vs. oxygen activity of donor-doped BaTiO₃ with nominal compositions: Ba_{0.99}La_{0.01}Ti_{0.9975}O₃ (V_{Ti}), Ba_{0.985}La_{0.01}TiO₃ (V_{Ba}) and Ba_{0.99}La_{0.01}TiO₃ (E) at 1200°C. Data are missing in the oxygen activity region of $-12 < \log a_{\text{O}_2} < -8$ due to extremely slow re-equilibration kinetics. The solid curve in (a) is the best fitted to Eq. (10) with Eq. (12) substituted in the text. The dotted curves are for visual guidance only.

species $k = \text{O}_2, \text{TiO}_2$, and K_j the mass-action-law constant for the associated reaction ($j = R, T, i$). It can be shown that the majority disorder types $n \approx 2[V_{\text{O}}^{\bullet}]; n \approx [La_{\text{Ba}}^{\bullet}]; [La_{\text{Ba}}^{\bullet}] \approx 4[V_{\text{Ti}}^{\prime\prime\prime}]$ of Eq. (5) lead

via Eqs. (2)–(4) to

$$n \propto a_{\text{O}_2}^{-m} \quad (6)$$

with $m = 1/6; 0; 1/4$, in turn, in accord with Eq. (1), see Fig. 1.

It is noted that the three specimens V_{Ti} (=Ba_{0.99}La_{0.01}Ti_{0.9975}O₃) E(=Ba_{0.99}La_{0.01}TiO₃) and V_{Ba} (=Ba_{0.985}La_{0.01}TiO₃) exhibit differences in magnitude particularly over the oxygen exponent region of $m \approx 1/4$ where the donors are believed to be electrically compensated by cation vacancies or $[La_{\text{Ba}}^{\bullet}] \approx 4[V_{\text{Ti}}^{\prime\prime\prime}]$ seemingly for the specimen V_{Ti}. The origin of the differences is not immediately clear, but seems to be related to a_{TiO_2} and/or $[La_{\text{Ba}}^{\bullet}] (\approx 4[V_{\text{Ti}}^{\prime\prime\prime}])$ depending on the initial compositions in the light of the relationship $n \propto a_{\text{O}_2}^{-1/4} a_{\text{TiO}_2}^{1/4} [La_{\text{Ba}}^{\bullet}]^{1/4}$ due to Eqs. (2)–(4). More work is required to elucidate this issue.

Nevertheless, there is essentially nothing new with the conductivity isotherms of Fig. 2(a), but it is not the case with the thermopowers, Fig. 2(b). As expected from the type of dopants (La_{Ba}^{\bullet}), the thermopowers have a positive sign¹ in accord with the majority carriers being electrons. However, it should be noted that the thermopower does first increase with decreasing oxygen activity from $a_{\text{O}_2} = 1$ while the conductivity increases rather monotonically. This fact indicates that there is a p-type contribution to some extent.

It is more clearly seen from a Jonker pear analysis [15]. For an n/p mixed conductor with transference numbers of t_n and t_p , respectively, the thermopower may be represented as (upper sign for $\theta \geq 0$; lower sign for $\theta \leq 0$)

$$\begin{aligned} \frac{e\theta}{k} &= \frac{e}{k}(t_n\theta_n + t_p\theta_p) = \mp \frac{1}{2}\varepsilon \left[1 - \left(\frac{\sigma_m}{\sigma} \right)^2 \right]^{1/2} \\ &+ \ln \left(\frac{\sigma}{\sigma_m} \right) \left\{ 1 \pm \left[1 - \left(\frac{\sigma_m}{\sigma} \right)^2 \right]^{1/2} \right\} + \frac{1}{2}\delta \end{aligned} \quad (7)$$

with

$$\varepsilon \equiv \frac{E_g}{kT} + A_n + A_p; \quad \delta \equiv \ln \frac{N_C b}{N_V} + A_n - A_p \quad (8)$$

where “ e ” is the fundamental charge, k the Boltzmann constant, σ_m the minimum conductivity where the electron conductivity exactly equals the hole conductivity ($\sigma_n = \sigma_p$), E_g the band gap, N_C and N_V the effective density of state at conduction and valence band edge, respectively, b the mobility ratio of electrons to holes

($\equiv \mu_n/\mu_p$), and A_n and A_p the constant kinetic term related to the entropy of transport of the carrier [9], respectively.

When $\sigma (= \sigma_n + \sigma_p) \gg \sigma_m$, Eq. (7) may be rewritten as:

(i) for $\sigma_n \gg \sigma_p$ (or $t_n \approx 1$)

$$\frac{e\theta_n}{k} \cong \ln \frac{\sigma_m}{\sigma} + \frac{1}{2}(\delta + \varepsilon) - \ln 2 = \ln \frac{N_C}{n} + A_n \quad (9a)$$

(ii) for $\sigma_p \gg \sigma_n$ (or $t_p \approx 1$)

$$\begin{aligned} \frac{e\theta_p}{k} \cong -\ln \frac{\sigma_m}{\sigma} + \frac{1}{2}(\delta - \varepsilon) \\ + \ln 2 = -\left(\ln \frac{N_V}{p} + A_p\right) \end{aligned} \quad (9b)$$

If the present systems were an exclusively n -type conductor or $t_n \approx 1$, $e\theta/k$ vs. $\ln \sigma$ would, thus, have to be linear with a slope of -1 [Eq. (9a)]. The experimental results are shown in Fig. 3 in comparison with Eq. (9a) (dotted line with a slope of -1). Obviously, the measured thermopower deviates from the theoretical slope of -1 as the conductivity decreases for all the speci-

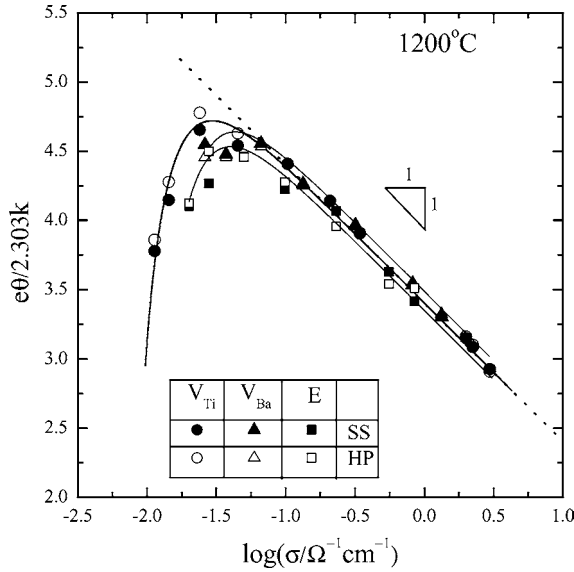


Fig. 3. Thermopower vs. conductivity for donor-doped BaTiO₃ with different nominal compositions: Ba_{0.99}La_{0.01}Ti_{0.9975}O₃ (V_{Ti}), Ba_{0.985}La_{0.01}TiO₃ (V_{Ba}) and Ba_{0.99}La_{0.01}TiO₃ (E). Solid symbols (●, ■, ▲) by the steady state technique (SS) and open ones (○, □, △) by the heat-pulse technique. The solid curves are the best fitted to Eq. (7) and dotted line with a slope of -1 is Eq. (9a) in the text.

mens, making the plot look like a half of a “pear.” This indicates that the p -type contribution grows more significant as the conductivity decreases with increasing oxygen activity as expected from Fig. 1.

The experimental data have been fitted to Eq. (7) for $\theta \geq 0$ quite satisfactorily as depicted by the solid curves. The best fitted values are $\sigma_m/S \text{ cm}^{-1} = (8.08 \pm 0.16) \times 10^{-3}$, $(11.2 \pm 0.5) \times 10^{-3}$, $(12 \pm 1) \times 10^{-3}$; $\varepsilon = 26.70 \pm 0.12$, 25.80 ± 0.15 , 26.3 ± 0.2 for the specimens V_{Ti}, E and V_{Ba}, respectively. Even if the kinetic parameters A_n and A_p are not precisely known a priori, one may safely guess that $E_g < 3.3$ eV due to Eq. (8), that is in agreement with the literature [16–18]. Nevertheless, the result for the specimen V_{Ti}, in particular, may be regarded as the most precise because the p -type contribution is the most extensive.

The conductivity of an electron/hole mixed conductor may be represented as [19, 20]

$$\sigma = \sigma_n + \sigma_p = \sigma_m \cosh\left(\frac{1}{2} \ln \alpha\right) \quad (10)$$

with

$$\alpha \equiv \frac{\sigma_p}{\sigma_n} \quad (11)$$

Obviously, $\sigma = \sigma_m$ when $\alpha = 1$. As the total conductivity σ and the minimum conductivity σ_m is known, the transference number of holes can be evaluated as $t_p = \alpha/(1 + \alpha)$. The results for the specimens V_{Ti}, V_{Ba} and E are all shown in Fig. 4. It is seen that the hole transference number takes a value up to $t_p = 0.15$ (V_{Ti}), 0.085 (E), and 0.057 (V_{Ba}) at the highest oxygen activity examined.

One may be interested in the value for oxygen activity where the conductivity minimum falls (i.e., $t_p = 0.5$). In the disorder regime of $m \approx 1/4$, the conductivity ratio may be written as

$$\alpha = \left(\frac{a_{O_2}}{a_{O_2}^*}\right)^{1/2} \quad (12)$$

where $a_{O_2}^*$ denotes the oxygen activity where $\sigma = \sigma_m$. Thus, $a_{O_2}^* = 32, 116, 308$ as $\alpha = 0.175, 0.093, 0.057$ at $a_{O_2} = 1$ for the specimens V_{Ti}, E and V_{Ba}, respectively. As the mobility ratio of electrons to holes is not much different from 1 at elevated temperatures [2, 21], approximately at $a_{O_2}^*$ falls the stoichiometric composition where $n = p$ and hence, $[La_{Ba}] = 4[V_{Ti}^{''}]$ due to Eq. (5). The origin of the differences in $a_{O_2}^*$ depending on the nominal compositions seems to be

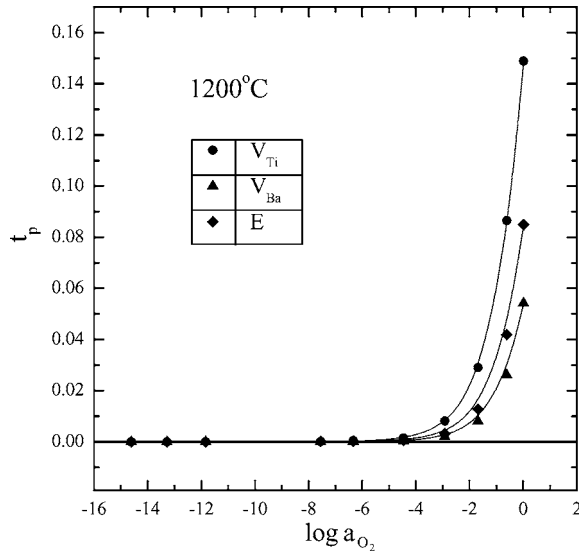


Fig. 4. Transference number of holes (t_p) vs. oxygen activity for donor-doped BaTiO₃ with the nominal compositions Ba_{0.99}La_{0.01}Ti_{0.9975}O₃ (V_{Ti}), Ba_{0.985}La_{0.01}TiO₃ (V_{Ba}) and Ba_{0.99}La_{0.01}TiO₃ (E). Solid lines are the calculated from Eqs. (10) and (12) in the text.

closely related to that of the differences in conductivity or $a_{O_2}^* \propto a_{TiO_2} [La_{Ba}^*]$, but yet to be elucidated.

Experimental fact, Eq. (12) in the stoichiometric regime where $[La_{Ba}^*] \approx 4[V_{Ti}'''] (\gg [V_{O}''])$ supports that $[V_{O}']$ be essentially independent of oxygen activity due to Eq. (2) and hence, a_{TiO_2} is essentially fixed in this region due to Eq. (3). It may suggest that the system is already a two phase mixture involving a neighboring phase to BaTiO₃.

4. Conclusion

It has been confirmed for donor-doped BaTiO₃ in complete thermodynamic equilibrium that in the region, where doped donors are believed to be electrically compensated by cation vacancies (e.g., $[La_{Ba}^*] \approx 4[V_{Ti}''']$), a *p*-type conductivity arises as $\sigma_p = \frac{1}{2} \sigma_m (\frac{a_{O_2}}{a_{O_2}^*})^{+1/4}$ in addition to majority *n*-type conductivity. For the nominal compositions, Ba_{0.99}La_{0.01}Ti_{0.9975}O_{3-δ} (V_{Ti}), Ba_{0.99}La_{0.01}TiO_{3-δ} (E) and Ba_{0.985}La_{0.01}TiO_{3-δ} (V_{Ba}) at 1200°C, the electron conductivity is expected to turn equal to the hole conductivity (i.e., $\sigma_n = \sigma_p$) at $a_{O_2}^* = 32$ (V_{Ti}), 120 (E) and 310 (V_{Ba}), where the total conductivity takes the minimum value of $\sigma_m \approx 0.01$ S/cm [respectively, 0.0081(V_{Ti}), 0.011(E) and 0.012 (V_{Ba}) S/cm]

and the increasing transference number of holes with the oxygen activity reaches $t_p = 0.15$ (V_{Ti}), 0.085 (E), and 0.057 (V_{Ba}) at $a_{O_2} = 1$. This fact confirms that the doped donors and cation vacancies are in the majority in the vicinity of the stoichiometric composition ($\delta \approx 0$) of the system and that the concentration of oxygen vacancies is essentially independent of oxygen activity in this regime, thus keeping a_{TiO_2} fixed. It is consequently suggested that donor-doped BaTiO₃ contains a second phase even in its stoichiometric regime.

Acknowledgments

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Note

1. In the present treatment, the thermopower is defined as $\theta = d\Delta\phi/dT$ in accord with Wagner [14] where $\Delta\phi$ stands for the thermovoltage, thus shows a + sign for an *n*-type conductor.

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