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Electrical transport properties of n-type $BaTiO_3$

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The electrical transport properties of $BaTiO_3$ are discussed against the background of recent defect-chemistry investigations and in the light of the small-polaron nature of the charge carriers. Seebeck-effect measurements and chemical investigations on highly doped $BaTiO_3$:La ceramics are also reported. It was found for $BaTiO_3$ that the dissociation energy required to set the conduction electrons free from their donor centers and also the kinetic-energy term of the small polarons contributing to the thermopower can be treated as negligible quantities.

I. INTRODUCTION

As in the case of most low-mobility materials, it has been debated for many years whether the charge carriers in n-type $BaTiO_3$ are small polarons[1,2] or band electrons.[3] Whereas it seemed at first that the optical and electrical properties could be interpreted either way, investigations in recent years[2,4,5] have revealed that the nature of the charge carriers cannot be explained consistently either in terms of band conduction or in the small-polaron picture.[6] In particular, the discussion is centered around the occurrence of a conductivity-dependent optical-absorption maximum at about 0.5 eV favoring small-polaron formation, the drift mobility of about 0.1–0.5 $cm^2/V\,sec$ being assumed to be too high for thermally activated small-polaron hopping, and the equivalence of drift and Hall mobility, which supports band conduction.

Explaining the electrical properties in terms of band conduction requires the assumption that the optical-absorption maximum is caused by electron excitation from donor levels (oxygen-vacancy levels as proposed by Berglund and Braun[3]) being about 0.3 eV below the conduction-band edge. However, extensive defect-chemistry investigations reported by several authors[5,7,8] give no indication of defect or impurity levels being in this range (see also the discussion in Ref. 6). On the other hand, when small polarons are assumed, the optical-absorption maximum gives a thermal activation energy for a small-polaron hop which is too high compared with the drift-mobility data given by $\mu \propto T^{-3/2}\exp(-\epsilon/kT)$.[6] The drift mobilities are known at[1,4] 200–300 K and[7] 1470 K; they are about equal to the measured and extrapolated Hall mobilities known between 200 and 1000 K.[5]

However, from the standpoint of small polarons, the available drift-mobility data are often called into question because the evaluation of the number of charge carriers necessary for determining the drift mobility from the dc conductivity ($\mu = \sigma/ne$) requires several assumptions about the Seebeck effect and defect chemistry from which the charge-carrier densities were deduced. In the defect-chemistry investigations it was assumed that there is complete ionization of the donors and a negligible kinetic-energy term was taken for the Seebeck coefficient. Both assumptions are under discussion from the viewpoint of small polarons as well as from that of band conduction. Debate centers in particular on the choice of the kinetic-transport term, which does not need to be zero even for small polarons (see Sec. III), and which was deduced to be about 2 to 3 in the case of band conduction (Berglund and Baer[3]).

In this paper, after discussing the small-polaron situation in $BaTiO_3$, we will present a comprehensive and critical recapitulation of the published drift-mobility investigations concerned with the small-polaron nature of the charge carrier and against the background of the recent defect-chemistry investigations on n-doped $BaTiO_3$.[7,8] We shall then report on our electrical experiments (Seebeck effect, conductivity) and chemical experiments (determination of the charge carrier by chemical analysis) on lanthanum-doped $BaTiO_3$ ceramics, the results of which confirmed the known drift-mobility values. We were also able in these experiments to determine the kinetic-energy term of the Seebeck coefficient and the dissociation energy required to excite an electron from the donor (lanthanum) neighborhood into an unbound small-polaron state; both quantities were found to be about zero, which provides additional support for the assumption of small polarons.

II. SMALL-POLARON SITUATION IN $BaTiO_3$

As was said at the beginning, the electrical conduction cannot be explained consistently either in the band model or in the small-polaron model. However, it was suggested in a preceding paper[6] that the results of the electrical and optical experiments are comparable if one assumes the existence of a small-polaron drift mobility which is enhanced with respect to the results of Holstein's nonadiabatic small-polaron hopping theory.[9]

The assumption of small-polaron hopping in $BaTiO_3$ seems to be reasonable from the estimation of Ref. 6 when the known drift-mobility values are used (these values are correct, as will be shown in the following sections). The transfer integral J was estimated to be 0.015 eV and the thermal-drift-mobility activation energy ϵ (being half of the polaron binding energy) to be about 0.023 eV. Although this satisfies the small-polaron formation condition[10] $J<4\epsilon$, it does not completely satisfy the applicability range of the nonadiabatic small-polaron hopping theory[11] $J^2<(\epsilon kT/\pi)^{1/2}\hbar\omega_0/\pi$ for $T>400$ K and[6] $\hbar\omega_0\approx 0.046$ eV [$J^2=2.25\times10^{-4}$ eV^2, the right-hand side of the inequality ranges from 2.3×10^{-4} eV^2 at 400 K to 4.6×10^{-4} eV^2 at 1470 K]. However, when Emin's[10] correlated small-polaron hopping is assumed (see below), where ϵ comes out to be about three times larger, the latter condition is slightly improved.

On the other hand, the conditions for adiabatic small-polaron hopping cannot be satisfied because the applicability condition is then governed by the above inequality in the opposite direction.[11] This reflects the fact that the small-polaron conduction in $BaTiO_3$ comes close to the so-called "transition" region[11] which is between the validity of the adiabatic and nonadiabatic theories.

It was suggested in a previous paper[6] that the small-polaron conduction in n-type $BaTiO_3$ can be understood qualitatively by assuming a drift mobility enhancement. In $BaTiO_3$ the conditions for a drift-mobility enhancement are fulfilled because the electron-phonon coupling constant deduced from the optical absorption, and also the calculated bandwidth of the longitudinal-optical phonon modes involved in the small-polaron formation, are both smaller than assumed by Holstein in his small-polaron theory.[6] These material properties both increase the drift mobility and lower the thermal activation energy for a small polaron hop.

de Wit[12] calculated that under these conditions the small-polaron hop rate is enhanced for quantum-mechanical reasons. He showed that in Holstein's nonadiabatic small-polaron theory the self-trapped electron has only one chance to tunnel to the neighboring site when two neighboring lattice sites are thermally excited (the "coincidence event") because this favorable ion configuration decays after only one lattice-oscillation period as a result of a broad dispersion of the longitudinal-optical phonons which form the polaron's polarization cloud. However, when the duration of the "coincidence event" is sufficiently long due to a small vibrational dispersion, then the probability of electron tunneling is greater than it is after the first or the following oscillation periods; this enhances the hop rate.

A drift mobility enhancement also results from Emin's theory of "correlated small polaron hopping."[10] In Emin's model, which describes a classical mechanism [it seems justified to assume classical hopping in $BaTiO_3$ in the temperature range above 400 K; $kT\gg J$ (Ref. 11)] two successive polaron hops are correlated with one another because the electron is able to hop to a third site before the initially occupied lattice site relaxes. At the limit of a very small vibrational dispersion, the drift mobility activation is reduced roughly to about one-third of the two-site hop value. Despite the higher energy necessary for a three-site coincidence, the drift activation energy is lowered because this event yields a greater hop probability than two two-site coincidences.

In the correlated hopping model, Hall and drift mobility need not be far from equal as is usually the case for uncorrelated small-polaron hopping. In particular, the ratio of Hall and drift mobility [$\mu_H/\mu_D\propto\exp(E_{\text{drift}}-E_{\text{Hall}})/kT$] is proportional to about $\exp(\epsilon/6kT)$ for the correlated situation, which is considerably smaller than the $\exp(2\epsilon/3kT)$ of the uncorrelated model[10] (uncorrelated model: $\epsilon=E_{\text{drift}}$). For $BaTiO_3$, where ϵ is already small ($\epsilon\cong0.063$ eV deduced from the mobility fit of Ref. 6), this gives an exponential term which is only 1.35 at 400 K and decreases to about 1.09 at 1470 K. Whereas the exponential term usually gives rise to the difference in the temperature slopes of drift and Hall mobilities, this is only of minor significance in $BaTiO_3$.

Furthermore the small-polaron situation in $BaTiO_3$ is close to the transition region where the Hall mobility is smaller than in the nonadiabatic region, as was discussed by Emin and Holstein[11] (in the adiabatic region the Hall mobility can become even smaller than the drift mobility at higher temperatures, or at $J<kT$,[11] as is the case in $BaTiO_3$). Thus, the assumption of comparable Hall and drift mobilities in $BaTiO_3$, which has been the strongest argument for band conduction in this material, need not be in contradiction with the assumption of small polarons.

III. PROBLEM OF EVALUATING THE DRIFT MOBILITY IN n-TYPE $BaTiO_3$

In one of their first papers on the polaron nature of electron conduction in n-type $BaTiO_3$, Gerthsen *et al.*[1] deduced the drift mobility in the room-temperature range from conductivity- and Seebeck-effect measurements on differently conducting $BaTiO_3$ polycrystals (ceramics) which were free from grain boundary resistivities. The charge-carrier density was derived from the Seebeck coefficient S, which is given by[13-15]

$$S=-(k/e)(\ln N_c/n+A) .$$

Here k denotes the Boltzmann constant, e is the electron charge, N_c is the (effective) polaron state density, n is the charge-carrier density, and A is the transport term, which is the energy per kT transferred by a small-polaron hop between the lattice sites involved.

Gerthsen *et al.*[1] put N_c equal to the titanium density of 1.55×10^{22} cm^{-3}. This is a reasonable choice because, as can easily be seen from band-structure considerations,[16,17] the small polarons are localized at the titanium sites. The lowest conduction bands originate from the ionic Ti^{3+} $3d^1$ levels and have their band minimum at the Γ point. However, an uncertainty arises because owing to the spin degeneracy,[14,15] one cannot exclude *a priori* a double occupation of the potential small-polaron site. In general, when a second (additional) electron is localized at a titanium site (chemically speaking, a quasi Ti^{2+} state) the Coulomb repulsion is reduced owing to further polarization of the lattice. This double occupation can be definitely discarded in the case of $BaTiO_3$ because the energy gain of about 0.25 eV,[2,6] due to the small-polaron binding, is too small compared with the Coulomb repulsion (Hubbard interaction), which is expected to be of the order of some electron volts at the titanium site.

However, somewhat more attention must be paid to the assumption of a vanishing transport term A, because $A=0$ holds only for the idealized case in which no account is taken of nonlinear electron-phonon interactions, anharmonicity of the lattice vibrations and changes in the force constants in the transition from the empty to the occupied state.[13] For a general case Austin and Mott[13] estimated A to be about $\frac{1}{20}\epsilon/kT$, where ϵ denotes the thermal hopping activation energy of the small polaron. From the optical absorption we obtain an upper limit of approximately 0.13 eV. Thus A is about 0.22 in the room-temperature range. This estimate, however, is based on Holstein's small-polaron model, and a treatment for the enhanced small-polaron hopping assumed to exist in n-type $BaTiO_3$ may yield different results. For example, in his correlated small-polaron hopping model, Emin[18] deduces an energy transfer even opposite to the carrier hop, because energy in his model is "absorbed primarily at the final site and emitted at the initial site." If we take $A=0.22$ as an upper limit, then the charge-carrier densities given by Gerthsen *et al.*[1] have to be multiplied by e^A, which is about 1.25. This correction, however, does not significantly alter the result that the drift mobility is about 0.5 to 0.6 cm^2/V sec in the room-temperature range and equal to the Hall mobility measured on the same samples. Negative A values, on the other hand, provide smaller charge-carrier densities, and hence drift mobilities higher than the Hall mobilities. Such a situation can occur in the case of adiabatic small-polaron hopping.[11]

Later on, Gerthsen *et al.*[4] extended their investigations on n-type $BaTiO_3$ polycrystals for which the charge-carrier density was deduced from thermogravimetric measurements. Treating undoped $BaTiO_3$ samples under different reducing conditions they obtained differently conducting samples. Every oxygen vacancy provided by this treatment contributed just one electron to the conduction, as was also found in the defect-chemistry investigations reported by Long and Blumenthal.[7] The plot of the electrical conductivity versus the oxygen vacancy density deduced from weighing (from about 6×10^{19} to 17×10^{19} cm^{-3}) then yields a drift mobility of 0.6 cm^2/V sec.

Because of experimental uncertainties, the authors could not definitely exclude the existence of a dissociation energy for the ionization of the oxygen vacancy. Taking into account, for example, an ionization energy of 80 meV, we estimate a donor exhaustion of about 80% for an oxygen vacancy concentration of 1×10^{20} cm^{-3}, and this delivers smaller effective charge-carrier densities and hence a drift mobility even higher than 0.6 cm^2/V sec, that is to say higher than the Hall mobility.

The drift mobility at 1470 K in lanthanum-doped $BaTiO_3$ was deduced to be about 0.1 cm^2/V sec.[8] This value was derived from conductivity investigations of differently doped polycrystals as a function of the oxygen partial pressure. In a distinct oxygen pressure range, the conductivity of the samples was found to originate solely from the conduction electrons contributed by the lanthanum donors. A plot of this conductivity versus the nominal lanthanum content delivered the drift mobility of 0.1 cm^2/V sec, which is about the value obtained from the extrapolation of the high-temperature Hall mobilities[5] (see also Fig. 1 in Ref. 6). However, the assumed complete ionization of the lanthanum donors holds only if the dissociation energy is of the order of some tenths of an electron volt. This choice for the dissociation energy and, hence, for the value of the drift mobility, is reasonable because it made it possible to explain the high-temperature conductivities and the defect chemistry of undoped and doped $BaTiO_3$ over several ranges of magnitude of oxygen partial pressures.[8]

From the equivalence of Hall and drift mobility at high temperatures, we conclude that in the room-temperature range, too, the drift mobility will not exceed the Hall mobility (in the adiabatic case μ_H/μ_D is a monotonic function of temperature[11]). With this conclusion we deduce from the thermopower measurements (see the discussion above) that we can reject negative A values not close to zero (small negative-transport terms cannot be excluded because of the scatter of the experimental data); furthermore the dissociation energy of the oxygen vacancies can also be assumed to be small.

Summing up, we conclude from the foregoing discussion that the mobility values obtained from the investigations described really represent the actual drift mobilities.

IV. ELECTRICAL AND CHEMICAL INVESTIGATIONS ON La-DOPED $BaTiO_3$

This section reports thermogravimetric, wet chemical, thermoelectrical, and electrical measurements on lanthanum-doped conducting $BaTiO_3$ ceramics which were carried out in order to obtain further confirmation of the results presented above and to elucidate the question concerning the dissociation energy required to separate an electron from its original lanthanum-donor site.

The thermogravimetric measurements were carried out at 1470 K at various partial pressures of oxygen on powder materials having La concentrations on the Ba sites of up to 10%. From the results of x-ray-intensity measurements on related perovskites such as[19] $Sr_{1-x}La_xTiO_3$ and[20] $Pb_{1-x}La_xTiO_3$ we deduced that in $BaTiO_3$, too, the big La ions only enter the Ba sites of the perovskite lattice. A detailed description of the thermogravimetric measurements can be found elsewhere,[21] so that here only the results of these investigations are briefly reported.

At distinct partial pressures of oxygen (depending on the temperature and the La concentration of the sample) the stoichiometric composition of the La-doped perovskite $BaTiO_3$:La corresponds to the chemical formula $Ba_{1-y}La_y^{3+}(Ti_{1-y}^{4+}Ti_y^{3+})O_3$. The "$Ti^{3+}$" has only to be interpreted in a stoichiometric sense, because one cannot define at this point where the electron is localized. This formula has already been reported by Eror and Smyth.[22] With increasing partial pressure of oxygen, the La donors are more and more compensated by the formation of electron-trapping vacancies on Ba sites (about 1.5 eV below the band edge) and therefore decreasing concentrations of the Ti^{3+} are found. With decreasing partial pressure of oxygen, on the other hand, singly ionized oxygen vacancies are formed and the number of Ti^{3+} ions will increasingly exceed that of the incorporated La^{3+}.

The concentrations of Ti^{3+} in the $BaTiO_3$:La was determined gravimetrically and was put equal to the carrier concentration at 1470 K. A theoretical electrical conductivity was then calculated using the drift mobility of Daniels and Härdtl[8] at 1470 K ($\mu = 0.1$ cm^2/V sec).

The electrical conductivity measured at 1470 K on the same material under the same oxygen pressure then proved to be nearly identical with the calculated conductivity over more then six ranges of the oxygen pressure. Thus we may conclude that at higher temperatures (1470 K) the numbers of the chemically determined Ti^{3+} and those of the charge carriers are identical.

At room temperature the concentration of Ti^{3+} in the $BaTiO_3$:La was determined in accordance with a method developed by Arend and Novak.[23] For these measurements densely sintered $BaTiO_3$:La ceramics having La concentrations of 0.5% to 4% on the Ba sites were reduced at 1470 K and thereafter quenched to room temperature. During cooling, very slight oxidation of the samples, which took place particularly at the grain boundaries, could not be completely prevented.[24] In most cases such prepared samples showed a too low electrical conductivity due to thin high-resistivity grain-boundary layers[25] (see the conductivity discussion at the end of this section and Table I). On the other hand, the measurement of the thermopower of such specimens is not influenced by nonconducting thin grain-boundary layers.[4]

After the measurement of the thermopower and the electrical conductivity, the samples were

TABLE I. Measured and calculated specific electrical conductivities. $\sigma_{\text{meas}} = G/R$, G is the geometrical factor; $\sigma_{\text{calc}} = n_{\text{electrical}} e \mu_D$.

Sample No. (see Fig. 1)	σ_{meas} (Ω^{-1}cm^{-1})	σ_{calc} (Ω^{-1}cm^{-1})
3	4.0	10.4
5	25.5	36.5
6	41.0	70.0

crushed to fine powders in an agate mortar. The powders were dissolved in amounts of 20–200 mg while stirring in 15 ml 20-vol% HCl, from which traces of O_2 and Cl_2 had been removed. The dissolution of the samples must be carried out in a protective gas atmosphere.

After complete dissolution of the samples, a solution containing a small number of Fe^{3+} ions was added. These Fe^{3+} ions were immediately reduced by the Ti^{3+} ions dissolved from the reduced $BaTiO_3$:La to the corresponding number of Fe^{2+} ions. The concentration of the Fe^{2+} ions was then colorimetrically determined in a dark room at a wavelength of 510 nm, using the red complex of the Fe^{2+} with 1, 10-phenanthroline in a buffer, the composition of which has been described in Ref. 23. The concentration of the Ti^{3+} in $BaTiO_3$:La could then be calculated from the concentration of the Fe^{2+} ions found in the solution. The experimental scatter of the chemically analyzed concentration of Ti^{3+} in $BaTiO_3$:La was found to be of the order 1×10^{18} Ti^{3+}/cm^3.

The thermopower was measured at room temperature in two different experimental arrangements. In one arrangement the specimens were fixed between two sinks in an air environment, and in the other they were placed in an oil bath with two heat-insulating chambers which could be separately heated. No difference was observed between the Seebeck data obtained from both methods. Figure 1 shows the chemically determined concentration of Ti^{3+}, which we denote by n_{chemical} versus the small polaron density n_s^0 which was deduced from the Seebeck effect assuming a zero transport term A (see Sec. III). Figure 1 reveals that the experimental data for densities below 6×10^{20} cm^{-3} are grouped around the bisector of the coordinates. From this behavior, information is derived about the magnitude of A and about the dissociation energy required to separate the electrons from their lanthanum centers where they originated.

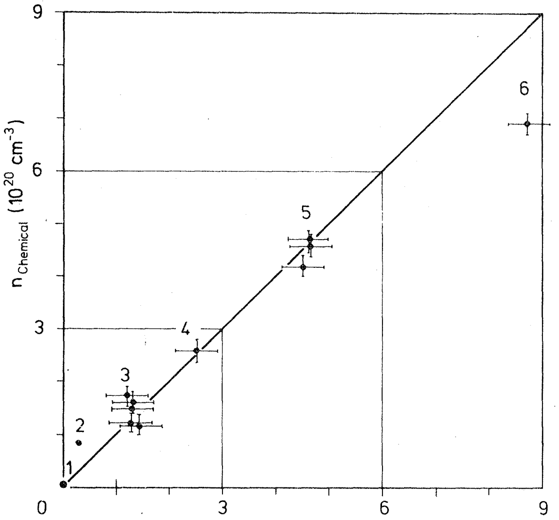

FIG. 1. Chemically determined charge-carrier density n_{chemical} vs the small-polaron density obtained from the Seeback coefficient by the use of $n_S^0 = N_c \exp(-e|S|/k + A)$ ($N_c = 1.55\times 10^{22}$ cm^{-3}, $A = 0$). The experimental points belong to samples having the following nominal lanthanum concentration (between parentheses the resulting charge-carrier concentration): (1) 0.005 (7.8×10^{19} cm^{-3}); (2) 0.006 (9.3×10^{19}); (3) 0.015 (2.3×10^{20}); (4) 0.02 (3.1×10^{20}); (5) 0.03 (4.7×10^{20}); (6) 0.04 (6.3×10^{20}). The figure shows that the reduction is not complete in the samples that have a lower lanthanum content.

We deduce from our chemical considerations that the density of electrons carrying the electrical current ($n_{\text{electrical}}$) cannot exceed n_{chemical} as long as we neglect electrons thermally excited from energy levels that lie deeper in the energy gap than the donor levels. The electrons coming from deeper states are associated with the oxygen orbitals; they are excited either from the p-type valence band (3.1 eV and gap) or from the oxygen orbitals enclosing a barium vacancy (about 1.5 eV below the conduction-band edge,[8] though we still may have to take into account a small amount of barium vacancies due to an incomplete chemical reduction process). However, considering the high activation energies of these electrons, it is obvious that not taking them into account is of no significance in the room-temperature range of our investigations. Thus $n_{\text{electrical}}$ will, in general, be smaller than n_{chemical}. Incidentally, we do not consider the case of the highly doped sample marked with the numeral 6 in the plot. For this composition the Seebeck effect yields higher charge-carrier values than allowed from the chemical analysis. It is possible that this deviation reflects the fact that in this concentration range the Seebeck coefficient can no longer be evaluated with the formula given in Sec. III. This formula is only valid for a sufficiently low density of small polarons that are not correlated with one another. We can summarize the relations between the relevant electron densities as follows:

$$n_S^0 = n_{\text{chemical}} \geq n_{\text{electrical}} = n_S^0 e^A .$$

Here the equality on the left-hand side represents the experimental results given in Fig. 1. This relation holds only for $A \leq 0$. The equality is obtained for $A = 0$, which results in a negligible dissociation energy.

A negative transport term A is compatible with the existence of a dissociation energy. From the defect-chemistry investigations at higher temperatures, a maximum dissociation energy of 0.1 eV can be presumed[8] for the lanthanum-doped $BaTiO_3$; this value gives an ionization degree of about 75% at room temperature for a donor density of 1.55×10^{20} cm^{-3}. However, a negative transport term significantly different from zero can be ruled out because this would deliver—see Sec. III—a drift mobility considerably higher than the Hall mobility in the room-temperature range. If a transport term exists that is different from zero, then we estimate A from the scatter of the available data to be in the range of $-0.1 \leq A \leq 0.1$. In particular, for $A = -0.1$ the charge-carrier densities evaluated from the thermopower experiments, assuming $A = 0$, have to be multiplied by about 0.9, which increases the room-temperature drift mobility by about 10%. This is compatible with a dissociation energy in the range of 50–60 meV.

However, we deduce from our experiments, and from the analysis of the previously published investigations, that in neglecting the transport term and the dissociation energy we obtain a sufficiently good approximation to the real physical situation in conducting $BaTiO_3$.

Having determined the charge-carrier density of our samples, it should now be a simple matter to derive the drift mobility from the electrical conductivity measurements. However, difficulties arise from the evaluation of the specific electrical conductivity because, as remarked at the beginning of this section, the materials are inhomogeneous owing to some oxidation at the grain boundaries. We therefore expect the effective measured specific conductivity of the specimens to be smaller than the specific conductivity of the conducting phase. The thermopower nevertheless represents the electrical properties of the grain interior and is not influenced by the grain boundary layers.[4] Table I gives a comparison between the specific electrical conductivities of our samples measured by a four-contact dc bridge technique, and values calculated from the thermopower derived charge-carrier densities and the room-temperature drift mobility of 0.5 cm^2/V sec. As expected, the calculated specific electrical conductivity observed is higher than the measured value.

V. SUMMARY

We have discussed in some detail the evaluations of the drift mobility given in the literature. Against the background of the recent knowledge of defect chemistry and the small-polaron nature of the charge carriers we were thus able to show that the drift mobility, which is known at 300–400 K and at 1470 K, is correctly given. The thermal activation energy deduced from these mobility values on the assumption of "ordinary" small-polaron hopping was the reason for assuming enhanced small-polaron hopping, because the thermal activation energy derived from the thermal mobility slope is considerably smaller than the activation energy derived from the optical measurements. Furthermore, it was shown that the equivalence of the measured Hall and drift mobilities can be understood in the light of the small-polaron assumption for $BaTiO_3$.

The drift mobility discussion and our investigations on the lanthanum-doped $BaTiO_3$ ceramics have shown that the kinetic-energy term is a small, possibly negative, quantity. This also supports the small-polaron explanation for $BaTiO_3$ because in the band conduction model a kinetic-energy term of about 2 to 3 had to be assumed. The dissociation energy required to set a conduction electron free from its donor site has also to be small. We conclude that it is good approximation to the physical reality in n-type $BaTiO_3$ to neglect the transport term as well as a possible dissociation energy. These results are also of significance for the investigation of positive-temperature characteristic resistivity (PTC) type $BaTiO_3$ ceramics that have grain-boundary resistivities, because the thermopower detects the electrical properties in the grain interior.[4] Thus, when the parameters entering the Seebeck coefficient expression are known, the thermopower measurements provide a simple and convenient method for determining the charge-carrier densities within the grains of polycrystals.

Whereas, generally, the electrical transport properties cannot be explained by electrical experiments alone, it is a favorable circumstance in the case of barium titanate that the nature of the charge carriers can be interpreted in the context of optical and electrical measurements, defect-chemistry investigations, and chemical analyses, performed on various monocrystalline and polycrystalline materials, doped and undoped. All these experiments consistently support the conclusion that the charge current in n-type barium titanate is carried by small polarons having an enhanced drift mobility due to correlation of successive polaron hops.

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