PART IV. THE KINETICS OF EQUILIBRIUM RESTORATION IN BARIUM TITANATE CERAMICS

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Abstract
The kinetic processes occurring with the equilibrium restoration have been investigated by means of dynamic conductivity measurements. The experiments, carried out in the temperature range from 700 to 1100 °C, show that equilibrium restoration is determined by the bulk diffusion of vacancies. In undoped and acceptor-doped BaTiO₃ the diffusion of oxygen vacancies starting from the surface of the sample is the most important process which is influenced neither by the type nor by the amount of the acceptor dopes. In donor-doped BaTiO₃, however, the diffusion of barium vacancies is decisive. Due to the special formation mechanism these vacancies diffuse from the grain boundaries into the bulk of the grains, so that the microstructure of the ceramic has an important effect on the establishment of equilibrium in these materials. In contrast to the barium vacancies the oxygen vacancies turn out to have exceptionally high diffusion coefficients, which have also been found with SrTiO₃.

1. Introduction

The answer to the question of what defect concentrations are present in a solid depends mainly on two factors. Firstly the concentrations of defects are determined by the thermodynamically or energetically most favourable state to which the solid tends, a state determined mainly by the thermodynamic constants. Secondly, but just as important, there is the question of whether such a state of equilibrium can be achieved at all in a finite time, and here in particular the kinetic processes of the actual reactions and diffusion processes are of decisive importance. If, for example, it is assumed that the time required for achieving equilibrium is long in comparison with the duration of the experiment, then it will hardly be possible to detect any changes in the physical properties (e.g. conductivity) in the period of measurement. This means that the measurements determine a quasi-equilibrium in which possibly not all kinds of defects have already attained their final state of equilibrium.

Even if the kinetic processes at elevated temperatures appear to play an important role only in rare cases, they are very decisive indeed with respect to defects prevailing at room temperature. Let us assume, for instance, that a ceramic specimen is completely in equilibrium with the surrounding gas atmosphere at the temperature of sintering; then on cooling, equilibria will be maintained down to a certain temperature, depending on the rate of cooling. But at that point the first kinds of defects (e.g. metal vacancies), will start to become
frozen because of kinetic inhibition, so that more or less heterogeneous distributions of defects are already formed then. Other types of defects (e.g. the oxygen vacancies) continue to remain in equilibrium with the surrounding atmosphere down to lower temperatures, so that their concentrations begins to freeze only later. This stepwise process continues until finally, at room temperature, the atomic defects are completely frozen and equilibrium restoration takes place only in the electronic system, i.e. the electronic charge carriers (electrons and holes) assume an equilibrium with the frozen, atomic defects. Hence at room temperature there will normally be very complex and heterogeneous distributions of defects, which become important particularly with respect to the conductivity, since often very small changes in the defect concentration may have a great effect on the semiconducting properties. In contrast to conductivity measurements at elevated temperatures, which in the case of BaTiO₃ show good agreement among the various authors¹,²,₃,⁴) there are large numbers of experimental results at room temperature which, partly for unexplained reasons, differ from each other by orders of magnitude. This poor reproducibility can be understood more easily if the kinetic processes are taken into account¹⁸). Because a number of kinetic parameters (e.g. rate of cooling) have so far been given inadequate attention and have therefore been taken into account either not at all or only rather schematically, it is hardly surprising that different results should be obtained with the different procedures.

For a better understanding of the defect-induced behaviour and of the semiconducting properties of BaTiO₃ the kinetics of the actual processes represent an essential aspect which has so far not been given sufficient weight. Since in the special case of BaTiO₃ the reaction between the gas phase and the solid is limited *) to the exchange of oxygen, this reaction and the related diffusion processes assume special importance. Such kinetic investigations should therefore have the oxygen vacancies as their starting point. They must, however, be extended to barium vacancies, because these vacancies play a special role in donor-doped barium titanate.

2. Experimental method, and evaluation

The diffusion of oxygen vacancies has been examined in, among other materials, SrTiO₃⁵,⁶,⁷) and Al₂O₃⁸) by different methods, while in the case of BaTiO₃ hardly any experimental data have been published up to now. In the selection of appropriate methods of investigation, the dynamic measurement of the conductivity⁶,⁸) appears particularly suitable, because here the oxygen partial pressure requires only a slight change in order to achieve easily detectable changes in the conductivity. Yet here, just as in the case of all other methods, some knowledge about the disorder must be available to permit of an

*) Because of the low vapour pressures of the barium and titanium cations.
unambiguous interpretation. Such knowledge is provided by the models \(^1,2,3,4\) developed in respect both of undoped and of donor-doped BaTiO\(_3\).

Basically the measuring procedure is, first of all, to bring a specimen into equilibrium at high temperature and a given oxygen partial pressure. Then after a while a conductivity constant with respect to time is established. Now if the oxygen partial pressure is changed discontinuously at constant temperature, then the conductivity tends, with a certain response function \(\sigma(t)\), to a new equilibrium value, as shown in fig. 1a. Normally, during this process, equilibrium is first established at the surface of the specimen by a corresponding reaction and then spread to the entire volume by diffusion processes. Here either the surface reaction or the diffusion process may determine the time required to achieve equilibrium.

For the determination of the diffusion coefficient, this measured response function \(\sigma(t)\) must be compared with a calculated one. Therefore, on the basis of the defect models \(^1,2,3,4\) calculations were made from which, by means of Fick's diffusion laws \(^9\), the calculated change in conductivity was obtained as a function of the dimensionless diffusion quantity \(D t/h^2\) (cf. appendix). In accordance with the geometry of the specimens, the diffusion equation was first of all solved with the boundary conditions valid for a flat plate of thickness \(h\) \(^9\). The result of this calculation, which is in agreement with the data given by Walters and Grace \(^6\) is shown in fig. 1b. The comparison of this calculated curve with the measured response function \(\sigma(t)\) was performed by means of a diagram \(^6\), illustrated in fig. 1c, in which some typical experimental results have been plotted. From the slope \(D/h^2\) of the straight lines and from the thickness of the specimen the diffusion coefficient \(D\) can be calculated. Two conditions,
Fig. 1b. Calculated response function after a change of the oxygen partial pressure.

Fig. 1c. $D t / h^2$ versus time for some representative experimental results. The $D t / h^2$ values are taken from the calculated response function and the corresponding $t$ values are obtained from the measured ones.

however, must be satisfied in order to obtain the right value. On the one hand the appropriate boundary conditions must be used for the solution of the diffusion equation, and on the other the diffusion process must be the rate-determining step in the establishment of equilibrium. If one of these conditions is not satisfied, an incorrect value of the diffusion coefficient will be calculated, which apparently depends on the specimen thickness $h$. Such a dependence allows us to check whether the right boundary conditions have been used (see below). Unless otherwise stated, the evaluation below will be based on the
boundary conditions of a flat plate of thickness $h$, in other words the assumption will be made that the decisive diffusion length $l_0$ is determined by the specimen thickness $h$.

Since the diffusion coefficients of the oxygen vacancies in SrTiO$_3$ single crystals are known from the literature, the measuring method was first checked with this material. In corresponding measuring conditions the values found are in good agreement both with the thermogravimetric results of Paladino and with the data of Walters and Grace.

Quite generally the restoration of equilibrium is brought about by the diffusion of charged defects. For that reason the measured value of the diffusion coefficient may be influenced in particular conditions by internal electric fields. The diffusion coefficients given in the present paper must therefore be interpreted first of all as ambipolar coefficients. As long as one is concerned merely with the question of the time needed for the attainment of equilibrium or of the concentration profile of the defects resulting from a special treatment, this problem is irrelevant, because only the ambipolar diffusion coefficients obtained by this measuring procedure are decisive with respect to the questions mentioned above.

For such measurements a sufficiently rapid change in the oxygen partial pressure is required, achieved here by a special design of the furnace. For this purpose the flowing gas, with an exactly defined oxygen partial pressure, is transported directly and without turbulence to the specimen via a thin tube of alumina. The conductivity is measured continuously by means of a four-point method with protruding Pt wires. The entire construction is mounted in a thyristor-controlled gas-tight furnace, the core of which is a Kanthal-wound alumina tube with brazed flanges of Remanit. Oxygen partial pressures were adjusted by means of well-defined gas mixtures ($N_2/O_2$ or CO/CO$_2$).

The test materials were ceramic specimens with dimensions of $15 \times 5 \times 0.5$ mm, the preparation of which is described in more detail elsewhere. As will be shown below, porosity and microcracks play a special role in the kinetic investigations. Care was therefore taken in the preparation to avoid microcracks. To improve the density, the specimens underwent an isostatic hot-pressing process developed by Härdtl, so that the final density of the specimens was better than 99% of the theoretical value.

3. Results of measurements and discussion

3.1. Undoped and acceptor-doped barium titanate ceramics

The question of deciding to what kind of defect the measured diffusion coefficients must be assigned may lead to some difficulty. Here the particular conditions with regard to the equation of electroneutrality are decisive, which can be derived from the defect models. In contrast to Daniels and Härdtl,
however, the author agrees with Long and Blumenthal [2]) that with undoped *) BaTiO$_3$ at high oxygen partial pressures ($P_{O_2} = 1$ atm) the neutrality condition

$$[A'] \approx 2[V_{O'}]$$ (1)

is valid, which would also explain the results of the high-temperature measurements [2,4]). In addition to the arguments of Long and Blumenthal [2), this assumption is supported by the following findings:

(a) In comparison with La-doped BaTiO$_3$, in which barium vacancies govern the electroneutrality, undoped BaTiO$_3$ attains equilibrium very much faster, so that here other defects must obviously have a determining influence (see below).

(b) Diffusion investigations by Paladino et al. [5,12]) have clearly shown that, in undoped SrTiO$_3$, the concentration of oxygen vacancies is fixed by acceptors, independently of temperature and oxygen partial pressure. This finding suggests an extrinsic disorder similar to eq. (1). Since BaTiO$_3$ and SrTiO$_3$ form closely related perovskite compounds, it may be assumed that similar conditions apply to BaTiO$_3$.

(c) In the case of undoped BaTiO$_3$ a comparison of the diffusion coefficients of oxygen vacancies with those coefficients obtained by means of tracer techniques leads to the same result as that found by Paladino et al. [5,12]) (see below).

Therefore it will be assumed in the following that in undoped and in acceptor-doped BaTiO$_3$ at high partial pressures the equation of electroneutrality is given by eq. (1). At present it is not possible to make any precise statements regarding the nature of the acceptors. Impurities **) as well as frozen metal vacancies $V_{Ba}$ and $V_{Ti}$ which are not in equilibrium with the gas atmosphere may be concerned. On all other points the author agrees with the statements of Daniels and Härdtl [1].

Since the measured response function $\alpha(t)$ is determined only by the major type of defect, the diffusion coefficients measured at high oxygen partial pressures ($P_{O_2} = 0.1–1.0$ atm) must be assigned to doubly ionized oxygen vacancies (cf. eq. (1)). The initial experimental investigations were prompted by the following questions:

(a) Is the equilibrium restoration of the disorder in BaTiO$_3$ a diffusion-controlled process?

(b) Does the preferred diffusion along grain boundaries play a special role in equilibrium restoration?

*) To avoid confusion it should be noted that in the present paper the expression "undoped" is used for materials which are prepared without deliberate doping additives. It is not excluded, however, that these "undoped" materials contain a certain amount of impurities acting for example as acceptors.

**) Originating in the raw materials or in the milling process.
(c) In what way does the porosity of the ceramic influence the process of equilibrium restoration?

To answer these questions, ceramic specimens of different thickness, different grain size, and different porosity were examined. In figure 2 the diffusion coefficients thus found have been plotted in the form of an Arrhenius diagram. Although these measurements were evaluated in the manner already described, for the sake of simplicity we shall discuss the above problems with a simplified method of evaluation which, however, is qualitatively identical with the method actually used (cf. sec. 2). If in solving the diffusion equation the boundary conditions of a flat plate of thickness $h$ are assumed, then it is possible in principle to calculate the diffusion coefficient $D$ by means of the formula given by Jost (ref. 9, p. 37):

$$D = \frac{k_1 h^2}{\tau},$$

(2)

with $k_1$ = a constant, obtained from the solution of the diffusion equation ($k_1 \approx 1/\pi^2$).

$h$ = thickness of specimen (decisive diffusion length),

$\tau$ = time constant of the measured response function $\sigma(t)$.  

![Fig. 2. Diffusion coefficients of the oxygen vacancies for specimens of different thicknesses, different grain sizes and different porosities.](image-url)
The use of eq. (2) is only justified, however, if a diffusion-controlled process is concerned in which furthermore the decisive diffusion length is determined by the thickness of the specimen. In the following it will be shown what deviations occur if one of these conditions is not met.

On the assumption that equilibrium restoration is a reaction-controlled process *), then the time constant $\tau$ is independent of the specimen thickness $h$. If eq. (2) is used nevertheless for the evaluation, one obtains a diffusion coefficient which seems to depend quadratically on the specimen thickness $h$. Another problem is the preferred diffusion along the grain boundaries, i.e. the oxygen is first of all transported very quickly to all grain boundaries in the specimen. Thereafter the slower process of bulk diffusion gets under way from the grain boundaries to the interior of the grains. In that case the diffusion equation must be solved to a first approximation, with the boundary conditions of a sphere, so that the time constant $\tau$ will be given by the following expression (see ref. 9, p. 46):

$$\tau = k_2 \frac{\phi^2}{D},$$

with $k_2 = a$ constant, obtained from the solution of the diffusion equation, $\phi = grain\ diameter\ (decisive\ diffusion\ length)$.

If in these conditions evaluation is still performed by means of eq. (2) again a diffusion coefficient $D_{app}$ is obtained which apparently displays a strong dependence on the specimen thickness and on the grain size:

$$D_{app} = \frac{k_1}{k_2} h^2 D.$$  

Figure 2 shows that, with the exception of specimen 306-11, the diffusion coefficient calculated by eq. (2) depends neither on the specimen thickness $h$ nor on the grain diameter $\phi$. According to the above considerations the following conclusions can be drawn from fig. 2:

(a) With respect to these measurements the correct boundary conditions have been used.

(b) Equilibrium restoration in BaTiO$_3$ is a diffusion-controlled process, in other words the surface reaction proceeds so fast that the surface is in equilibrium with the surrounding gas atmosphere at all times.

(c) Grain-boundary diffusion does not play any role in equilibrium restoration. This latter result, however, holds only with respect to the diffusion of oxygen vacancies. Since the self-diffusion coefficient measured by means of tracer atoms depends also on the concentration of vacancies (see below, eq. (6)), a preferential diffusion of these tracer atoms along the grain boundaries may be possible, if it

* E.g. by the surface reaction: O(lattice) $\rightleftharpoons V_o + \frac{1}{2} O_2(gas)$. 
is assumed that the concentration of vacancies at the grain boundaries is higher than inside the bulk.

Quite considerable deviations are found in fig. 2 with respect to specimen 306-11. This material is a $\text{BaTiO}_3$ ceramic which was sintered at lower temperatures, so that the ceramic produced was not yet dense. With its density of about 85% of the theoretical value, this material has a marked (open) porosity, which exerts a decisive effect on the diffusion behaviour. In such specimens the oxygen completely penetrates via the pores into the material, just as in a sponge, so that the decisive diffusion lengths are greatly diminished. If the above boundary conditions are applied, then by analogy with eq. (4) an apparently too high value of the diffusion coefficient is obtained. If the decisive diffusion length is estimated by comparison with specimen 301-12, one obtains a value of about 35 $\mu$, which accords in order of magnitude with the mean distance between pores of specimen 306-11. This result shows how important it is to use dense materials for such investigations. In any event the occurrence of open pores must be avoided, and the same applies to microcracks.

Figure 3 once again represents the individual measured values of the diffusion

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**Fig. 3.** Diffusion coefficient $D_V$ of the oxygen vacancies and self-diffusion coefficient $D_{TR}$ for $\text{BaTiO}_3$ ceramic.
coefficient of doubly ionized oxygen vacancies. Because the oxygen partial pressure was varied in these experiments between 0.1 and 1.0 atm in either direction, two values are obtained for the diffusion coefficient, which are denoted as in- and out-diffusion of oxygen. Both values are in good agreement with one another 4). These results can be represented in the form

\[ D_V = 5.7 \cdot 10^3 \exp(-(2.05 \text{ eV}/kT)) \text{ cm}^2/\text{s}. \] (5)

Comparison of these diffusion coefficients of the oxygen vacancies \( D_V \) with the tracer measurements of Doskocil 13 reveals, as shown in fig. 3, that the self-diffusion coefficient \( D_{TR} \) is some 3 to 4 orders of magnitude smaller than \( D_V \). Since \( D_{TR} \) and \( D_V \) are related 5) by

\[ D_{TR} = \frac{[V_{O_{tot}}]}{[C_O]} D_V, \] (6)

with \([V_{O_{tot}}] = \text{oxygen vacancies per cm}^3\),
\([C_O] = \text{oxygen lattice sites per cm}^3\).

the results are in accordance with expectations *). At temperatures of 900°C or less, \( D_{TR} \) and \( D_V \) have the same energy of activation, 2 eV. With respect to eq. (6) this agreement can be interpreted only if the concentration of oxygen vacancies is fixed by acceptors, independently of the temperature. Similar results were found by Paladino et al. 5.12) in respect to SrTiO\(_3\). The energy of activation 2 eV must therefore be interpreted as the enthalpy of motion.

From the quotient \( D_{TR}/D_V \) the acceptor concentration 2) \([A_{tot}] \approx [A']^2 \) can be estimated by means of eq. (1) and (6), which, on referring to fig. 3, leads to a value \([A_{tot}] \approx 1.7 \cdot 10^{19} \text{ cm}^{-3} \) for the material of Doskocil 13). This result is of a plausible order of magnitude in respect of the technical grade BaTiO\(_3\) ceramic used by Doskocil 13). For the energy of activation, 0.5 eV, occurring in the range 900°C < \( T < 1100°C \) it was not possible to find a satisfactory explanation, since little information is available concerning the material used by Doskocil.

The effect of various dopes on the diffusion behaviour is illustrated in fig. 4. All the dopes to which fig. 4 refers are additions which are incorporated as acceptors in the cation lattice. The low doping concentrations of 0.2 at % were chosen intentionally, on the one hand to avoid difficulties in sintering (high porosity), and on the other to ensure the use of monophasic materials. It will be seen in fig. 4 that the results largely accord with the values given above in respect of undoped BaTiO\(_3\) (specimen 301-12). Apart from Cu- and Mn-doped 4) Eq. (6) is applicable only if the elementary diffusion mechanism is governed by an interchange of sites via vacancies. This condition is certainly satisfied by perovskite compounds 4). Then eq. (6) implies that a tracer atom can jump only if it happens to be adjacent to a vacancy, while the vacancy always finds an exchange partner in the regular lattice atoms.
Fig. 4. Diffusion coefficient of the oxygen vacancies for BaTiO$_3$ ceramics containing various dopes of acceptors.

BaTiO$_3$, both of which differ slightly from the behaviour of the undoped material, the effect of acceptor doping on the diffusion coefficient seems to be small, at least at low concentrations. Since the results with respect to Ga-doped BaTiO$_3$, which was investigated up to doping concentrations of 1.6 at $\%$, show no deviations either, it is assumed that the other dopes will behave similarly at higher concentrations. These experiments show that the condition of electroneutrality regarding acceptor doping in the range of 0–1.6 at $\%$ obviously remains unchanged. The establishment of equilibrium is therefore always governed by the same type of defect ($V_0^\cdot$). Since the diffusion of the oxygen vacancies takes place in the anionic lattice, while the dopes here used are incorporated in the cationic lattice, an appreciable change in the value of the diffusion coefficient is also unlikely, so that the results here found are largely as expected.

3.2. Donor-doped barium titanate ceramics

Quite a different picture is obtained when donors are incorporated in BaTiO$_3$. The results of doping with 0.5 at $\%$ lanthanum are illustrated in fig. 5 with respect to two specimens of different thicknesses. Fig. 5a reveals some noticeable
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differences from the earlier results. Apart from the change in the energy of activation, now 2.8 eV, the most striking aspect is the very much smaller value of the diffusion coefficient. Furthermore the results reveal a dependence on the thickness of the specimen, which in accordance with eqs (2), (3) and (4) allows the only possible interpretation, that in this case the decisive diffusion length is not, as assumed in the evaluation, correlated with the specimen thickness. These results, which at first sight are quite incomprehensible, will now be discussed in more detail.

Although the interpretation of a thickness dependence on account of surface reactions or grain-boundary diffusion, mentioned above in sec. 3.1, can in principle be applied in this case also, it is hard to understand from a physical point of view how such low doping concentrations can have such a decisive effect on the properties of the surface and the grain boundaries. A much more plausible explanation results from a close examination of the atomic disorder in this material. Very detailed investigations by Daniels and Härdtl ¹) concerning the conductivity properties of La-doped BaTiO₃ have shown that in the conditions *) in which the measurements of fig. 5 were in fact carried out, the lanthanum dope is compensated mainly by barium vacancies:

\[ 2[V_{Ba^{IV}}] \approx [La^+] . \]  

(7)

![Graphs showing diffusion coefficient of barium vacancies](image)

Fig. 5. Diffusion coefficient of the barium vacancies.
(a) evaluated with the boundary conditions of a flat plate \( l_0 = h \) (wrong values).
(b) evaluated with the boundary conditions of a sphere \( l_0 = \phi = 2\mu \) (correct values).

*) \( P_{O_2} = 0.1 - 1.0 \) atm, \( T < 1200 \) °C.
These investigations showed also that in this range of the partial pressure the oxygen vacancies have no effect on the conductivity. The response function \( \sigma(t) \) is therefore caused not by the diffusion properties of the oxygen vacancies but by the diffusion of barium vacancies. This fact, while able to explain the lower values of the diffusion coefficient and the change in the activation energy, does not provide any information about the thickness dependence found in the fig. 5a. To solve this problem, the mechanism by which barium vacancies are formed has to be considered in more detail (cf. also Smyth).

Since the low vapour pressure of barium rules out any vaporization of barium atoms, the formation of barium vacancies can only take place if the barium atoms released by this process can find new sites of incorporation. Formation of barium vacancies will therefore be possible only by means of the following mechanisms:

(a) New \( \text{BaTiO}_3 \) lattice cells can be formed at the specimen surface, and in these the released barium atoms can then find new sites. This mechanism, however, requires the simultaneous formation and diffusion of titanium vacancies, because the formation of \( \text{BaTiO}_3 \) lattice cells also requires titanium atoms.

(b) The same process as in (a) above can occur at the grain boundaries.

(c) At the grain boundaries of these materials one often finds traces of a second phase, which because of the titanium excess added during the process of preparation may be due to the formation of higher titanates (e.g. \( \text{BaTi}_3\text{O}_7 \)). A reaction of released barium atoms with such titanium-rich foreign phases may also facilitate the formation of barium vacancies. A conceivable reaction scheme, which should, however, be considered only as an example, might be the following:

\[
\begin{align*}
2 \text{Ba(lattice)} & \rightleftharpoons 2 \text{Ba} + 2 \text{V}_{\text{Ba}}, \\
\text{BaTi}_3\text{O}_7 & + 2 \text{Ba} + 2 \text{O} \rightleftharpoons 3 \text{BaTiO}_3, \\
2 \text{O(lattice)} & \rightleftharpoons 2 \text{V}_\text{O} + 2 \text{O},
\end{align*}
\] (8)

or written in one equation

\[
\text{BaTi}_3\text{O}_7 + 2 \text{Ba(lattice)} + 2 \text{O(lattice)} \rightleftharpoons 3 \text{BaTiO}_3 + 2 \text{V}_{\text{Ba}} + 2 \text{V}_\text{O}.
\]

(d) At the grain boundaries the released barium ions may form a barium-rich phase, e.g. \( \text{Ba}_2\text{TiO}_4 \). That implies a scheme of reactions similar to eq. (8) above.

Although, at present, the details of the mechanism by which the barium vacancies are formed and annihilated have not yet been clearly established, it is nevertheless possible to state that the alternatives (a) and (b), on account of the fact that the diffusion of titanium ions is strongly hampered, are less probable than a mechanism of the type mentioned in (c) or (d). The two latter
cases involve a floating interface between the BaTiO$_3$ and the foreign phase which can be shifted, either towards the bulk of the grain or towards the foreign phase, depending on the particular state of disorder. With such a formation of barium vacancies at the grain boundaries, the defect equilibrium is established by diffusion of the barium vacancies from the grain boundaries to the interior of the grain, so that in this case the decisive diffusion length $l_D$ is given by the grain diameter $\phi$. The results in fig. 5a have been obtained on the assumption of the boundary conditions of a flat plate ($l_D = h$). Since with the formation of barium vacancies at the grain boundaries this assumption is no longer applicable, one ought in accordance with eq. (4) to expect a diffusion coefficient that depends strongly on the thickness of the specimen. This dependence is confirmed by the data given in fig. 5a.

It remains to clarify the causes of the formation or annihilation of barium vacancies at the grain boundaries if the gas atmosphere is changed at the surface. Here the oxygen vacancies, with their much more rapid diffusion than that of the barium vacancies *) control the formation of barium vacancies by slight shifts of their equilibrium concentration. The details of such a equilibrium restoration would be that, after a change of the oxygen partial pressure, first of all the concentration of oxygen vacancies assumes a new value which, because of their rapid diffusion, becomes quickly established throughout the entire specimen. In the condition of electroneutrality, however, the oxygen vacancies play only a negligible role, so that this step would not lead to any appreciable change in the conductivity. The entire reaction shown in eq. (8) implies a mass-action law of the form

$$[V_{Ba}] [V_O] = K_S,$$

so that the changed concentration of the oxygen vacancies leads to a corresponding shift in the equilibrium of the reaction equation (8), and this in turn causes the formation (or annihilation) of barium vacancies. Detailed calculations have shown that the amount of oxygen necessary for the formation of barium vacancies can easily be transported by the rapid diffusion of oxygen vacancies through the bulk. Therefore the assumption of oxygen diffusing along the grain boundaries is not necessary. Then the barium vacancies thus formed diffuse from the grain boundaries to the bulk of the grain, until the new equilibrium has been established. Since the conductivity is mainly determined by barium vacancies, it is only this latter step which leads to an appreciable change in the conductivity.

*) Because the oxygen vacancies diffuse in the anionic lattice, while the incorporation of lanthanum takes place in the cationic lattice, it may be assumed that the establishment of the oxygen vacancies in La-doped BaTiO$_3$ takes place at a rate similar to that in undoped material. Then, according to eqs (5) and (10) the diffusion coefficients of $V_{Ba}$ and $V_O$ at 1200 °C differ from each other by a factor of 10$^7$. 
The diffusion initiated at the grain boundaries requires completely new boundary conditions for the diffusion equation. On the assumption of spherical grains these new boundary conditions imply that the decisive diffusion length is now given by the grain diameter \( l_b = \phi \). Since in fig. 5a these new boundary conditions have not yet been taken into account, the evaluation carried out there is no longer valid. The values shown in fig. 5a are therefore wrong. The correct values, obtained with the new boundary conditions, are represented in fig. 5b. The new method of evaluation now leads to the same diffusion coefficient with respect to either specimen. These results can be represented in the form of *):

\[
D_{VBa} = 6.8 \cdot 10^{-2} \exp \left( -2.76 \frac{eV}{kT} \right) \text{cm}^2/\text{s}. \tag{10}
\]

This finding, which confirms that the diffusion of barium vacancies starts at the grain boundaries, is in agreement with the results of investigations concerning the behaviour of La-doped BaTiO\(_3\) on oxidation. While fine-grained material \((\phi \approx 2 \mu)\) at 1100°C was completely oxidized in air after just a few hours **), coarse-grained specimens \((\phi \approx 100 \mu)\) could not be oxidized even after several days of heat treatment at 1100°C. Scattered coarse-grained regions in the fine-grained material did not permit of oxidation either, and manifested themselves as dark spots even after many days of heat treatment. The following estimate will show that the oxidation times are also of the right order of magnitude. With \( T = 1100°C \) a diffusion coefficient \( D = 5.5 \cdot 10^{-12} \text{cm}^2/\text{s} \) is obtained from fig. 5b. With a grain size of 2 \( \mu \) diameter the time necessary for oxidation is \( \tau_0 \approx \phi^2/D = 2 \) hours. With \( \phi = 100 \mu \), on the other hand, one finds \( \tau_0 \approx 210 \) days. Since a similar behaviour was also found with Sb-doped BaTiO\(_3\), these kinetic results are most probably applicable to all BaTiO\(_3\) ceramics containing donor dopes.

This strong dependence of the equilibrium restoration on the grain size may possibly explain the results of Seuter 3) who found that with donor-doped BaTiO\(_3\) no equilibrium could be obtained at high oxygen partial pressure. Unfortunately he gives no information about the grain size of the materials used, but it is very probable that his materials were coarse-grained. If this is correct the long time necessary for equilibrium restoration is caused by these large grains. At low oxygen partial pressures, however, Seuter 3) was able to attain equilibrium with all materials in spite of coarse grains. This can be explained by the fact that the conductivity at low partial pressure is determined by oxygen vacancies 1), so that under these conditions equilibrium is achieved

*) Since now the grain size is represented by a squared term in the evaluation, as in eq. (3), an important role is played by the inaccuracy in the determination of the grain size, so that the absolute values of the diffusion coefficients shown in fig. 5b are subject to a corresponding error.

**) Recognizable by the bright yellow colour of previously bluish-black specimens.
very much faster because of the high diffusion coefficient found for oxygen vacancies.

4. Conclusion

(a) The investigations of the defect kinetics have shown that the equilibrium restoration in BaTiO$_3$ is determined by diffusion processes. In contrast to the barium vacancies, the oxygen vacancies turn out to have exceptionally high diffusion coefficients. This finding accords qualitatively with expectations in the case of a perovskite lattice structure, because the arrangement of the oxygen ions in the octahedron is most favourable for an interchange of lattice sites $^4$). Because the titanium ions at the centre of the oxygen octahedron are fully screened in all directions, it may be assumed that their diffusion is greatly impeded and that titanium vacancies, if present at all, remain frozen up to very high temperatures.

(b) In undoped and acceptor-doped BaTiO$_3$ equilibrium restoration is determined by the diffusion of the oxygen vacancies. Neither the type nor the amount of the acceptor dopes are then of much importance.

(c) In donor-doped BaTiO$_3$, however, the diffusion of barium vacancies is decisive. Because of their special formation mechanism these defects start to diffuse from the grain boundaries. Accordingly the microstructure (grain size, foreign phases) has an important effect on the establishment of equilibrium in these materials.

(d) These latter results are of great importance on the semiconducting properties at room temperature. In particular the formation of poorly conducting grain-boundary layers and the dependence of the resistivity on the doping concentration can be understood much better if the kinetic processes of equilibrium restoration are taken into account. These problems, which are very important with respect to PTC-resistors and intergranular capacitors, will be discussed in more detail elsewhere $^{17,18}$).

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Appendix $^*)$

These calculations are carried out on the following assumptions:

(a) The surface reaction proceeds very much faster than the diffusion process.

(b) The acceptors are incorporated homogeneously.

(c) The oxygen partial pressure is changed only by a small amount.

In the simplified equation of neutrality (1) only the two major types of defects have been taken into account. If one considers also the next important type, the electroneutrality at high oxygen partial pressure is given by the following

$^*$) For the sake of simplicity the defect concentrations are given here without brackets.
equation 2)

\[ A' = 2 V_{o''} + p. \]  \hspace{1cm} (A1)

From this the electrical conductivity can be derived

\[ \sigma = e \mu p = e \mu (A' - 2 V_{o''}). \]  \hspace{1cm} (A2)

After changing the oxygen partial pressure by a small amount a concentration profile of oxygen vacancies will be formed which can be calculated by solving the diffusion equation. For a thin plate of thickness \( h \) one obtains 9)

\[ V_o(x, t) = V_o^\infty + \]

\[ + (V_o^0 - V_o^\infty) \sum_{i=0}^{\infty} \frac{4}{\pi(2i+1)} \sin \left( \frac{\pi (2i+1) x}{h} \right) \exp \left[ -\pi^2(2i+1)^2 \frac{D t}{h^2} \right] \]

with

\[ V_o^\infty = V_o(t = \infty), \]
\[ V_o^0 = V_o(t = 0). \]  \hspace{1cm} (A3)

With eq. (A2) the corresponding conductivity profile can be calculated

\[ \sigma(x, t) = e \mu [A' - 2 V_{o''}(x, t)]. \]  \hspace{1cm} (A4)

Since only the mean value \( \bar{\sigma} \) of the conductivity can be measured by four-point methods we have to integrate this expression in the following way

\[ \bar{\sigma}(t) = \frac{1}{h} \int_0^h \sigma(x, t) \, dx. \]  \hspace{1cm} (A5)

After some further calculation steps one obtains the normalized conductivity

\[ \frac{\bar{\sigma} - \sigma_0}{\sigma_\infty - \sigma_0} = 1 - \sum_t \frac{8}{\pi^2 (2i+1)^2} \exp \left[ -\pi^2(2i+1)^2 \frac{D t}{h^2} \right] \]

with

\[ \sigma_0 = \sigma(t = 0), \]
\[ \sigma_\infty = \sigma(t = \infty). \]  \hspace{1cm} (A6)

This normalized conductivity is represented as a function of \( D t/h^2 \) in fig. 1b. A similar calculation can be performed for other geometries (e.g. sphere) or for other conditions of electroneutrality. In the case of La-doped BaTiO_3 we have to start from the equation

\[ \text{La':} \quad 2 V_{Ba'''} + n \]  \hspace{1cm} (A7)

which, however, yields the same result as in eq. (A6). A more sophisticated derivation is given by the author (see ref. 4).
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18) R. Wernicke, to be published.