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Nonstoichiometric Disorder in Single-Crystalline $BaTiO_3$ at Elevated Temperatures*

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The electrical conductivity of single-crystalline $BaTiO_3$ was measured over the temperature range 800–1200°C while in thermodynamic equilibrium with oxygen partial pressures from 10^0 to 10^{-19} atm. The behavior was consistent with the presence of barium and oxygen vacancies, due to the inherent BaO deficiency of the crystal, combined in the form of neutral defect complexes. The *n*-type electrical conductivity indicated the formation of additional, fully ionized oxygen vacancies while the *p*-type disorder resulted from the partial filling of oxygen vacancies present to compensate the accidental acceptor impurity content. This model takes into account two factors which are commonly ignored in ternary oxides: (1) Deviations from ideal cation–cation stoichiometry may result in substantial concentrations of defects; (2) in close-packed structures with multivalent cations and substantial band gaps, the enthalpies of formation for intrinsic defects are so unfavorable that impurity-related defects will be dominant in the near-stoichiometric region.

There have been several studies of the defect chemistry of $BaTiO_3$ by means of equilibrium electrical conductivity measurements made on polycrystalline and flux-grown samples at temperatures above 500°C (*1–6*). All of these studies indicate that there is an extensive range at low oxygen pressures (P_{O_2}), where the conductivity increases with decreasing P_{O_2}, characteristic of *n*-type conduction related to oxygen deficiency, whereas in the P_{O_2} range near 1 atm, the conductivity increases with increasing P_{O_2}, characteristic of *p*-type conduction related to a stoichiometric excess of oxygen.

Equilibration in these two characteristic regions has a clear impact on the room-temperature electrical properties. $BaTiO_3$ which has been equilibrated with a reducing atmosphere is a dark-colored *n*-type semiconductor at room temperature with resistivities as low as 10 ohm cm (*7*), while after equilibration with an oxidizing atmosphere such as air or oxygen, it is a light-colored *p*-type insulator with resistivities of the order of 10^{12} ohm cm (*8*).

The structural analogs $SrTiO_3$ and $CaTiO_3$ have not been studied in as much detail, but appear to be quite similar. In both cases the equilibrium conductivity increases with de-

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creasing P_{O_2} in the region of low P_{O_2} (*9*, *10*). Neither has been studied while in equilibrium with P_{O_2} near 1 atm, and no equilibrium behavior characteristic of *p*-type conduction has been reported. $CaTiO_3$ has been reported to be *p*-type at room temperature, presumably after exposure to oxidizing atmospheres (*11*).

In this study, the high-temperature, equilibrium conductivity of a $BaTiO_3$ single crystal grown from a TiO_2-rich melt (*12*) has been measured. Thus the possible complications related to flux-derived impurities (*13*) or to the grain structure of polycrystalline material have been avoided.

Experimental

The experimental procedure has been described previously (*14*) except that CO/CO_2 metered gas mixtures were used to establish the oxygen partial pressures below 10^{-5} atms. The $BaTiO_3$ single crystal was grown from the two-phase region, $BaTiO_3(s)$ plus liquid, on the TiO_2 excess side of stoichiometry in order to avoid the high-temperature hexagonal form of $BaTiO_3$ (*12*). The crystals grown in this way are undoubtedly on the excess titanium side of stoichiometry, but any such excess is smaller than can be determined reliably by chemical analysis. The chemical analysis of impurities is given in Table I.

Results and Discussion

The electrical conductivity of single-crystalline $BaTiO_3$ in the temperature range 800–1200°C and in equilibrium with oxygen partial pressures ($Ar–O_2$ mixtures) between 10^{-5} and 1 atm is shown in Fig. 1. As can be seen, the electrical conductivity shifts from *p*-type to *n*-type as P_{O_2} is decreased.

TABLE I

ANALYSIS OF $BiTiO_3$ CRYSTAL[a]

Element	Weight %
Si	~0.001
Fe	~0.001
Mg	~0.001
Cu	~0.001
Al	~0.0001
Sn	~0.0001
Mn	~0.0001

[a] Ca, Zr, Sr, Nb, Co, Zn, Na, Bi, Pb, Cd, and Ag not detected.

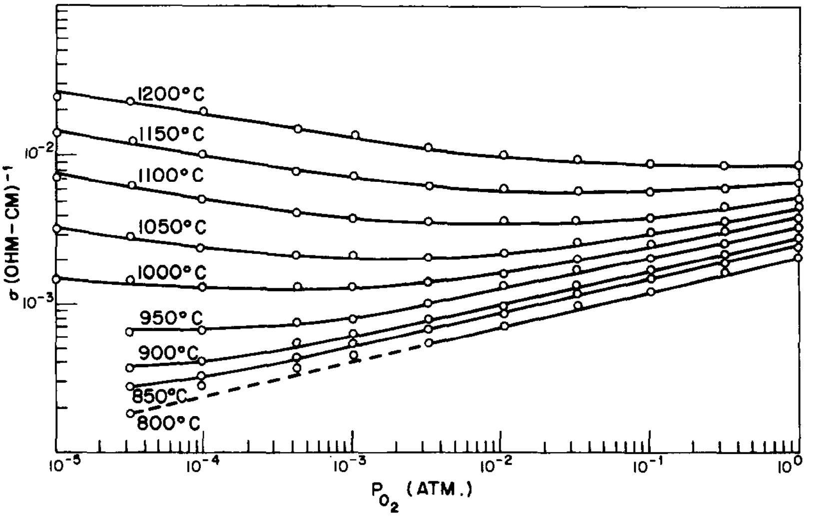

FIG. 1. The conductivity of single-crystalline $BaTiO_3$ as a function of oxygen pressure at constant temperature, from 10^{-5} to 10^0 atm.

The n-type electrical conductivity of $BaTiO_3$ was extended to lower oxygen partial pressures by employing CO/CO_2 mixtures over the temperature range 900–1200°C, and these data are shown in Fig. 2. The log σ vs log P_{O_2} data are linear for as many as 10 decades of oxygen partial pressure for a given temperature. This very extensive region of linearity affords the opportunity to determine the defect model responsible for the n-type electrical conductivity. A slope of approximately $-\frac{1}{6}$ is found for the log σ vs log P_{O_2} data at the higher temperatures and a slope of nearly $-\frac{1}{5}$ for the 900°C data. These data are given in Table II.

TABLE II

P_{O_2} DEPENDENCE OF CONDUCTIVITY AND ARRHENIUS SLOPES FOR THE n-TYPE REGION

T (°C)	m for $\sigma_n \propto P_{O_2}^{-1/m}$
900	5.17 ± 0.04 or 5.58 ± 0.06 for lower P_{O_2} points
950	5.75 ± 0.05
1000	5.92 ± 0.02
1050	5.89 ± 0.02
1100	5.92 ± 0.01
1150	6.08 ± 0.04
1200	6.15 ± 0.03

P_{O_2} (atm)	Arrhenius slopes (kcal/mole)
10^{-6}	46.6 ± 0.9
10^{-7}	45.0 ± 0.6
10^{-8}	44.6 ± 0.4
10^{-9}	45.2 ± 0.3
10^{-10}	44.9 ± 0.3
10^{-11}	44.6 ± 0.3
10^{-12}	44.1 ± 0.4
10^{-13}	44.3 ± 0.3
10^{-14}	44.5 ± 0.5
10^{-15}	44.2 ± 0.6
10^{-16}	43.8 ± 0.5

The n-Type Region

The slope of $-\frac{1}{6}$ is similar to that found for $SrTiO_3$ (*9*) and $CaTiO_3$ (*10*) as well as to the results of Long and Blumenthal (*3*), Seuter (*5*), and Chan and Smyth (*6*) for polycrystalline $BaTiO_3$. Yamada and Miller have determined the carrier concentration by Hall effect measurements for single-crystalline $SrTiO_3$ quenched from equilibrium with various oxygen partial pressures, and they found a similar relationship between the electron concentration and the equilibrium partial pressure

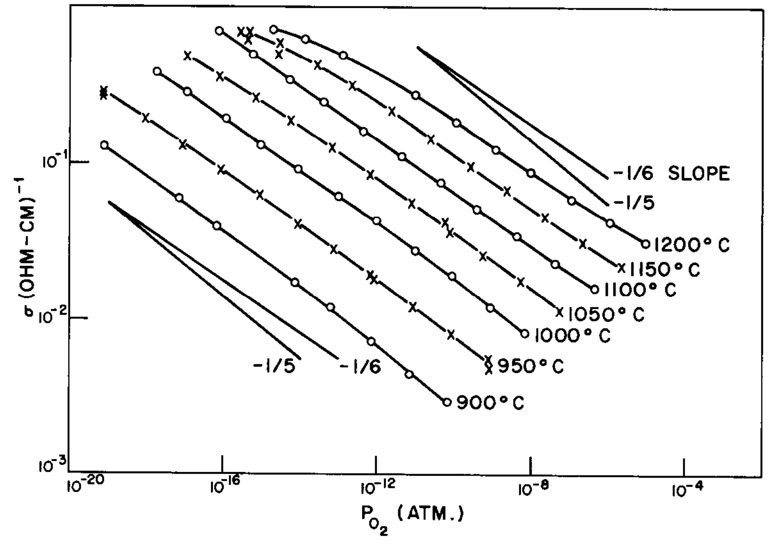

FIG. 2. The conductivity of single-crystalline $BaTiO_3$ as a function of oxygen pressure at constant temperature, from 10^{-20} to 10^{-5} atm.

(*15*). These same authors found that the relative densities of the quench samples were in good agreement with the presence of one oxygen vacancy for every two electrons, indicating that oxygen vacancies are fully (doubly) ionized at room temperature and above.

The three polycrystalline samples of $BaTiO_3$ used by Long and Blumenthal were found to be 2.1, 4.6, and 6.0 mole% deficient in BaO by chemical analysis (*3*). They noted no systematic variation of the equilibrium conductivity among these samples. Seuter found that addition of TiO_2 to his polycrystalline material had no marked influence on the resistivity, while addition of 1.5 mole% BaO shifted the *p–n* transition to slightly higher P_{O_2} (*5*). Chan and Smyth maintained precise control over the cation content of their samples during the synthesis step (*6*). A comparison of a sample having an ideal cationic ratio with one 0.1 mole% deficient in BaO showed no major differences in the equilibrium conductivity values. The crystal used in this study was pulled from a TiO_2-rich melt in order to lower the solidus temperature below that of the disruptive hexagonal to cubic transition (*12*); its composition should thus correspond to some place on the TiO_2-rich phase boundary, depending on the final temperature of equilibration. Rase and Roy were convinced that there is a definite phase width on the TiO_2-rich side and show a boundary at about 1 mole% excess TiO_2 at 1400°C (*16*). The study of sintering kinetics as a function of Ba/Ti ratio by Anderson suggests a phase width of the same order (*17*).

Deviations from the ideal Ba/Ti ratio must be accommodated by point defects. A number of mechanisms can be envisioned for the incorporation of TiO_2 into $BaTiO_3$ of ideal composition, including

$$TiO_2 \rightleftharpoons Ti_I^{\cdot\cdot\cdot\cdot} + 2O_I'', \qquad (1)$$

$$TiO_2 \rightleftharpoons Ti_I^{\cdot\cdot\cdot\cdot} + 4e' + O_2, \qquad (2)$$

$$2TiO_2 \rightleftharpoons Ti_{Ba}^{\cdot\cdot} + Ti_{Ti} + 3O_O + O_I'', \qquad (3)$$

$$2TiO_2 \rightleftharpoons Ti_{Ba}^{\cdot\cdot} + Ti_{Ti} + 3O_O + 2e' + \tfrac{1}{2}O_2, \qquad (4)$$

$$TiO_2 \rightleftharpoons Ti_{Ti} + 2O_O + V_{Ba}'' + V_O^{\cdot\cdot}, \qquad (5)$$

$$TiO_2 + \tfrac{1}{2}O_2 \rightleftharpoons Ti_{Ti} + 3O_O + V_{Ba}'' + 2h^{\cdot} \qquad (6)$$

Equations (2), (4), and (6), which generate electronic defects, can be excluded because of the observed lack of effect of the Ba/Ti ratio on the electronic conductivity. Both $Ti_I^{\cdot\cdot\cdot\cdot}$ and O_I'' are unfavorable defects, so Eq. (5), involving the formation of V_{Ba}'' and $V_O^{\cdot\cdot}$, is the most probable choice. This is in accord with the density measurements of Yamada and Miller which showed that $V_O^{\cdot\cdot}$ is the preferred defect for oxygen deficiency in $SrTiO_3$ (*15*), and the observation of Eror and Smyth that an equivalent oxygen deficiency compensates for any cation deficiency built into donor-doped $BaTiO_3$ (*18*). The equilibrium incorporation reaction, Eq. (5), can be characterized by a mass-action expression

$$[V_{Ba}''][V_O^{\cdot\cdot}] = K_5 a_{TiO_2} \qquad (7)$$

where a_{TiO_2} is the equilibrium activity of TiO_2.

When oxygen deficiency is also incorporated into such a system by reducing the oxygen activity in equilibrium with the BaO-deficient $BaTiO_3$, we should consider

$$O_O \rightleftharpoons \tfrac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e' \qquad (8)$$

and

$$[V_O^{\cdot\cdot}]n^2 = K_8 P_{O_2}^{-1/2}, \qquad (9)$$

where $n \equiv [e']$. It is clear that a substantial built-in BaO deficiency will initially exceed the disorder from the oxygen loss described in Eq. (8). For this case the electrical neutrality condition will read

$$[V_{Ba}''] \approx [V_O^{\cdot\cdot}] \approx K_5^{1/2} a_{TiO_2}^{1/2}. \qquad (10)$$

From Eqs. (9) and (10) we can then obtain

$$n \approx \frac{K_8^{1/2}}{K_5^{1/4} a_{TiO_2}^{1/4}} P_{O_2}^{-1/4}. \qquad (11)$$

The data in Fig. 2 and Table II clearly indicate that at low P_{O_2} the electrical neutrality condition should be

$$n \approx 2[V_0^{\cdot\cdot}] \tag{12}$$

to give

$$n \approx (2K_8)^{1/3}P_{O_2}^{-1/6} \approx K_{13}P_{O_2}^{-1/6}\exp(-\Delta H_n/3RT), \tag{13}$$

where ΔH_n is the enthalpy of reaction for Eq. (8). For Eq. (12) to hold the oxygen deficiency must greatly exceed the built-in BaO deficiency.

The thermogravimetric work of Panlener and Blumenthal (*19*) indicates a maximum value of about 10^{-2} for x in $BaTiO_{3-x}$ for the most extreme conditions used in this study, and values more than an order of magnitude less than this for conditions well within the region of $\sigma \propto P_{O_2}^{-1/6}$ dependence. The weight changes observed by Seuter do not extend to quite as low a P_{O_2}, but appear to indicate even smaller values of x (*5*). Chemical analyses by Arend and Kihlborg (*20*) for $BaTiO_3$ reduced in hydrogen for 1 hr at 1275°C, a much more stringent reducing condition, gives $x = 3.6 \times 10^{-3}$. The conductivity data suggest values at least 50 times less than the maximum value of x for the high-pressure side of Fig. 2. Thus for Eq. (12) to be a valid expression for the dominant charged defects, no other charged defect can be present in excess of about 2×10^{-5} to 2×10^{-4} per cation site (20–200 ppm atomic). This is in vivid contrast with the preceding discussion that indicates that the BaO deficiency amounts to at least parts per thousand. This seeming contradiction is removed if it can be assumed that the defects related to the BaO deficiency are associated into neutral complexes, such as vacancy pairs, to such an extent that the residual, isolated, charged defects from this source do not affect the condition of charge neutrality, Eq. (12), and thus have no influence on the oxygen-deficient defect chemistry. This association can be represented as

$$V''_{Ba} + V_0^{\cdot\cdot} \rightleftharpoons (V''_{Ba}V_0^{\cdot\cdot}), \tag{14}$$

$$\frac{[(V''_{Ba}V_0^{\cdot\cdot})]}{[V''_{Ba}][V_0^{\cdot\cdot}]} = K_a(T) = K'_a \exp(-\Delta H_a/RT), \tag{15}$$

where ΔH_a, the enthalpy of association, is a negative number for this exothermic process. It is shown in the Appendix that $-\Delta H_a > 2$ eV is required for the association to be sufficiently advanced in the experimental temperature range of up to 1200°C, and that this is not an unrealistic magnitude.

An indication of the magnitude of ΔH_n, the enthalpy of the oxygen extraction reaction, is typically obtained from Arrhenius plots of the conductivity, as deduced from Eq. (13). This procedure neglects contributions from the temperature dependences of the carrier mobility or density of states. Arrhenius plots from the region of validity of Eq. (13) are shown in Fig. 3 and the slopes are listed in Table II. The average slope of 1.93 eV (44.5

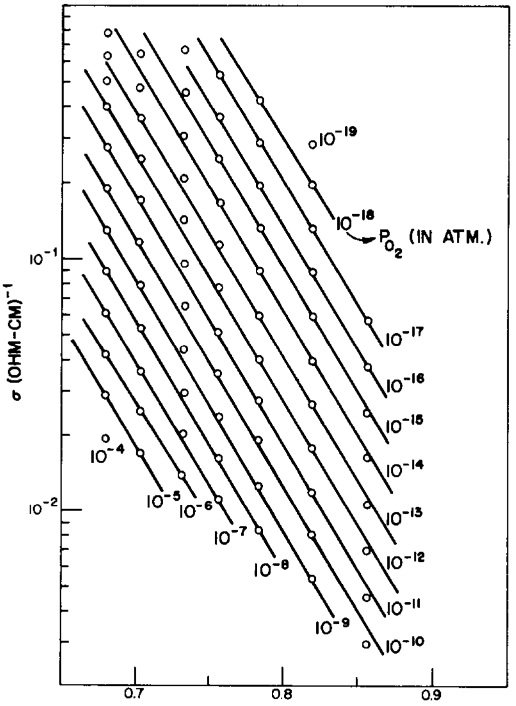

FIG. 3. Temperature dependence of conductivity of single-crystalline $BaTiO_3$ in the *n*-type, oxygen-deficient region.

kcal/mole) agrees well with the value of 43.8 kcal/mole reported by Long and Blumenthal (*4*). Neglecting the other temperature dependences, this gives a value of 5.79 eV (133.5 kcal/mole) for ΔH_n. Yamada and Miller determined a value for ΔH_n of 5.76 ± 0.20 eV for $SrTiO_3$ (*15*). This was based on a direct measurement of n by the Hall effect.

Seuter has determined the mobility of electrons in this temperature range by a combination of the Hall effect and conductivity (*5*). He describes the temperature dependence as T^{-1}, but the data are equally well represented by the classical $T^{-3/2}$ dependence for lattice scattering. This implies band conduction and K_8 in Eqs. (9) and (13) should thus contain N_c^2, the square of the density of states near the conduction band edge. The full expression for the Arrhenius slope of the electron conductivity at very low P_{O_2} is thus

$$\frac{\partial \ln \sigma_n}{\partial (RT)^{-1}} = \frac{\partial \ln \mu_n}{\partial (RT)^{-1}} + \frac{\partial \ln N_c^{2/3}}{\partial (RT)^{-1}} - \frac{\Delta H_n}{3}. \qquad (16)$$

For $\mu_n \propto T^{-3/2}$ and $N_c \propto T^{3/2}$ the μ_n and N_c terms in Eq. (16) result in an additive correction to ΔH_n of $\frac{1}{2}RT - RT$ or about 0.2 eV. If $\mu \propto T^{-1}$, as suggested by Seuter, the corrections cancel.

Transition Region

Arrhenius plots of the conductivity minima may be used to estimate the band gap of $BaTiO_3$ at 0°K, E_g°. The log σ_{min} data in Fig. 4 indicate a value of 3.27 eV (75.3 kcal/mole). This is in good agreement with the value of 3.3 eV reported from optical absorption data (*21*) on single-crystalline $BaTiO_3$ grown in the same laboratory as our crystal, and the value of 3.1 eV reported for polycrystalline $BaTiO_3$ (*5*). Assuming band conduction for both electrons and holes, the full expression for the Arrhenius plots is

$$\frac{\partial \ln \sigma_{min}}{\partial (RT)^{-1}} = \frac{\partial}{\partial (RT)^{-1}} \left[\frac{\ln \mu_n \mu_p}{2} + \ln N_c N_v \right] - \frac{E_g^\circ}{2}. \qquad (17)$$

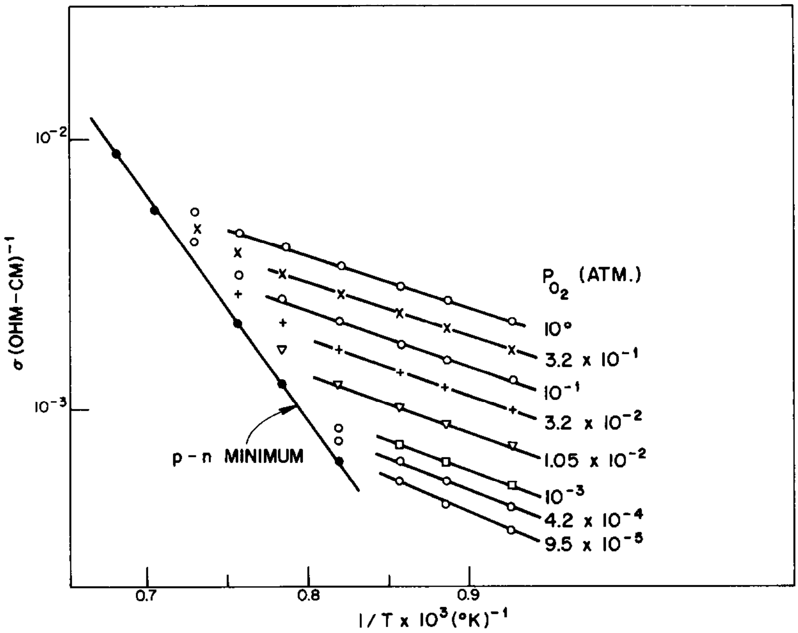

FIG. 4. Temperature dependence of conductivity of single-crystalline $BaTiO_3$ in the *p*-type, oxygen-excess region. Temperature dependence of the conductivity minimum is also shown.

There is no information available on the temperature dependence of the hole mobility, but if it is the same as for electrons, and if both N_c and N_v, the density of states near the valence band edge, are proportional to $T^{3/2}$, the mobility and density of states terms exactly cancel each other, and the Arrhenius slope is directly proportional to E_g°.

p-Type Region

$BaTiO_3$ seems to be the only representative of the alkaline earth titanates for which detailed equilibrium studies in the region of *p*-type conduction have been made (*1–6*). The materials studied have been of widely different character, but in all cases the conductivity increased with increasing oxygen pressure in the vicinity of 1 atm, in the temperature range 600–1200°C, indicative of *p*-type, or oxygen excess, conductivity.

The conductivity data obtained with Ar–O_2 mixtures in the range $10^{-5} < P_{O_2} < 1$ atm are shown in Fig. 1. The region of linearity in the *p*-type region increases in width with decreasing temperature as the *p–n* transition moves to lower P_{O_2}. The slopes of the pressure dependence given in Table III indicate that the values are trending toward $\frac{1}{4}$ with decreasing temperature where the range of linearity is greatest. Arrhenius plots of the data at constant oxygen pressure are shown in Fig. 4, and the activation enthalpies of conduction derived from the slopes are also given in Table III. A value of about 9.5 kcal/mole (0.41 eV) appears to be typical.

TABLE III

P_{O_2} DEPENDENCE OF CONDUCTIVITY AND ARRHENIUS SLOPES FOR THE *p*-TYPE REGION

T (°C)	m for $\sigma_p \propto P_{O_2}^{1/m}$
800	4.17 ± 0.07
850	4.23 ± 0.07
900	4.37 ± 0.08
950	4.68 ± 0.07
1000	5.32 ± 0.05
1050	6.12 ± 0.09
P_{O_2} (atm)	Arrhenius slopes (kcal/mole)
1.0	8.5 ± 0.06
3.2×10^{-1}	8.87 ± 0.09
10^{-1}	9.54 ± 0.08
3.2×10^{-2}	9.70 ± 0.10
1.03×10^{-2}	9.61 ± 0.44
3.2×10^{-3}	10.2 ± 0.2
10^{-3}	9.95 ± 0.28
4.2×10^{-4}	10.6 ± 0.7
Band gap 75.3 ± 0.4 kcal/mole	

It is apparent that a stoichiometric excess of oxygen can be incorporated into these $BaTiO_3$ crystals by a remarkably favorable process. In contrast to this low value, enthalpies of oxygen addition for a large number of rare earth and alkaline earth oxides are of the order of 3–6 eV (*22*), and the enthalpy of the oxygen extraction reaction for $BaTiO_3$. Eq. (8), was given above as 5.79 eV.

It is conceivable that these materials never contain a stoichiometric excess of oxygen, but have predominant *p*-type conduction for oxygen-deficient compositions, where the concentration of electrons still exceeds that of holes, only because the hole mobility is much greater than the electron mobility. However, Seuter found the hole mobility to be significantly less than that of electrons (*5*). Moreover, the manometric data of Conger and Anderson clearly show a minimum in the oxygen nonstoichiometry in the same region of P_{O_2} as the minimum conductivity values observed here (*23*). This model is therefore discarded as unrealistic.

The BaO deficiency makes available systematic oxygen vacancies which might accommodate a stoichiometric excess of oxygen without the need of creating a crystallographic excess.

$$(V''_{Ba}V_0^{\cdot\cdot}) + \tfrac{1}{2}O_2 \rightleftharpoons O_0 + V'_{Ba} + h^{\cdot}, \quad (18)$$

$$\frac{[V'_{Ba}][p]}{[(V''_{Ba}V_0^{\cdot\cdot})]} = K_{18}(T)P_{O_2}^{1/2} = = K'_{18}P_{O_2}^{1/2}\exp(-\Delta H_p/RT). \quad (19)$$

The discussion of relative defect concentrations given earlier suggests that $[(V''_{Ba}V_0^{\cdot})]$ can be taken as constant in Eq. (19) for a given composition. The unassociated barium vacancy that results when the oxygen vacancy in the neutral barium vacancy–oxygen vacancy complex is filled must be singly ionized in order to lead to the $\frac{1}{4}$ oxygen pressure dependence of the electrical conductivity data when Eq. (19) is combined with the corresponding charge neutrality condition

$$[V'_{Ba}] \approx p, \tag{20}$$

which is consistent with a slight excess of total vacant barium sites compared with the total number of vacant oxygen sites. The combination of (19) and (20), however, indicates that p and therefore the conductivity in this region should be proportional to $[(V''_{Ba}V_0^{\cdot})]^{1/2}$. No such variation has been noted. In particular, Chan and Smyth compared samples prepared to have Ba/Ti of 0.995 and 1.000, whereby the concentration of the divacancy complex should have differed by at least two orders of magnitude (*6*). The conductivity for the latter samples were higher by only about 30%, which is even in the wrong direction according to the above model, which must therefore be discarded.

One other source of oxygen vacancies is possible: those necessary to compensate for a net excess of an unknown, negatively charged impurity, i.e., an acceptor impurity such as Al'_{Ti}, which we shall generalize as A'. Thus the condition of charge neutrality in the near-stoichiometric region can be

$$2[V_0^{\cdot\cdot}] = [A'] \tag{21}$$

and the oxygen incorporation reaction could be

$$V_0^{\cdot\cdot} + \tfrac{1}{2}O_2 \rightleftharpoons O_0 + 2h^{\cdot}, \tag{22}$$

$$\begin{aligned}\frac{[p]^2}{[V_0^{\cdot\cdot}]} &= K_{22}(T)P_{O_2}^{1/2}\\ &= K'_{22}P_{O_2}^{1/2}\exp(-\Delta H_A/RT).\end{aligned} \tag{23}$$

Combination of (21) with (23) gives

$$p = \left(\frac{K'_{22}[A']}{2}\right)^{1/2} P_{O_2}^{1/4}\exp(-\Delta H_A/2RT) \tag{24}$$

as long as an insignificant fraction of the impurity-related oxygen vacancies have been filled. This fits the observed pressure dependence in this region, assuming that the trend toward shallower slopes at higher temperatures represents an intrusion of the transition region leading to the conductivity minima which are moving toward higher P_{O_2} with increasing temperature. On the basis of this model, ΔH_A should be twice the value of the activation enthalpies given in Table III, or 19 kcal/mole (0.82 eV). If the hole mobility has a temperature dependence of $T^{-3/2}$, and if K_{22} contains N_v^2, as expected for band conduction, the corrections to ΔH_A from these terms cancel. The ready availability of unassociated oxygen vacancies in this model explains the very low enthalpy of oxygen incorporation.

Long and Blumenthal earlier invoked the presence of an unknown acceptor impurity in order to explain their very similar experimental results (*4*). Seuter proposed that excess V''_{Ba}, related to a nonideal Ba/Ti ratio, acted as a constant background acceptor concentration (*5*). The lack of effect of variable Ba/Ti observed by Chan and Smyth disagrees with this suggestion (*6*), which does not lead to a consistent model in any case. The latter authors have studied the effects of deliberate additions of acceptor and donor impurities and concluded that their undoped material had an accidental net acceptor excess of about 130 ppm (atomic) (*6*). They proposed that all undoped material studied to date had a net excess of acceptor impurities, and attributed this to the fact that potential acceptor elements are naturally much more abundant than potential donor impurities. These impurities and their charge compensating partner, $V_0^{\cdot\cdot}$ in this case, will dominate the charge neutrality condition in the near-stoichiometric region because the concentrations of intrinsic defects, both ionic and electronic, should be very small in $BaTiO_3$, and the defects related to nonideal Ba/Ti ratio are associated into neutral complexes. Thus the only region where impurity-insensitive behavior is observed is in the range of lowest P_{O_2} and highest temperature where the conductivity varies as $P_{O_2}^{-1/6}$ and the $V_O^{\cdot\cdot}$ generated by Eq. (8) exceed those present due to the acceptor impurity.

From this model, one would expect the P_{O_2} dependence in the oxygen-deficient region just below the *p–n* transition to be derived from a combination of (9) and (21) to give

$$n \approx \left\{\frac{2K_8}{[A']}\right\}^{1/2} P_{O_2}^{1/4}. \qquad (25)$$

Data from this region are not available from this study, or from Long and Blumenthal, because of the gap in oxygen pressures between the highest achievable with $CO–CO_2$ mixtures, and the lowest available with $Ar–O_2$ mixtures. Chan and Smyth were able to bridge this gap by means of an electrochemical oxygen pump and activity detector based on calcia-stabilized ZrO_2 (*6*). They found the dependence of conductivity on P_{O_2}, temperature, and added acceptor impurities to be in good accord with Eq. (25). Seuter also observed an extensive range of $P_{O_2}^{-1/4}$ dependence even with $CO–CO_2$ mixtures (*5*), presumably because of greater acceptor impurity content of his samples.

The pressure and temperature dependences, as well as the absolute values, of the electrical conductivity agree very well among the four major studies of $BaTiO_3$. When the conductivities are compared in the impurity-insensitive region, e.g., at 1000°C and $P_{O_2} = 10^{-16}$ atm, all four values fall within the range 0.22 ± 0.03 ohm^{-1} cm^{-1}. This striking agreement between the single crystal used in this study and the polycrystalline material used in the other three studies indicates that grain boundaries have no significant effect on electronic transport in this range of experimental conditions, and that the results of such experiments on polycrystalline $BaTiO_3$ are typical of the bulk of the crystal.

Summary of the Defect Model

The defect chemistry of undoped $BaTiO_3$ is dominated by accidental acceptor impurities and the related oxygen vacancies, Eq. (21), except at the lowest P_{O_2} and highest temperatures where oxygen vacancies and electrons generated by oxygen deficiency become the dominant defects, Eqs. (8) and (12). Intrinsic ionic disorder never plays a significant role because of the high ionic charges and the lack of suitable interstitial sites. The band gap is sufficiently high to keep intrinsic electronic disorder below the net acceptor impurity contents of currently available material.

The defects related to BaO deficiency, presumed to be V_{Ba}'' and $V_O^{\cdot\cdot}$, are electrostatically associated into uncharged complexes, Eq. (14), and have no detectable effect on the defect chemistry of samples having a net excess of acceptor impurities.

The *p*-type conductivity observed near $P_{O_2} = 1$ atm results from a stoichiometric excess of oxygen which occupies the impurity-related oxygen vacancies, Eq. (22). Thus a stoichiometric excess of oxygen is achieved even while not all of the available oxygen sites are occupied. This points out the distinction between stoichiometric and crystallographic excesses. The ready availability of unbound oxygen vacancies results in an unusually low enthalpy for the oxygen addition reaction, Eq. (22).

Appendix

The defect model described in this paper implies that the concentrations of free barium and oxygen vacancies resulting from dissociation of the associated complex are substantially less than the 100-ppm range estimated for the acceptor impurity, and thus can be neglected in the condition of charge neutrality. From Eq. (15) we can estimate the value of ΔH_a necessary to keep the concentration of dissociated vacancies below the 10-ppm level for the experimental temperature range. Kröger has reviewed published parameters for defect association and shows that the entire preexponential term in association relationships such as Eq. (15), i.e., the entropy factor, is generally close to unity (*24*). At the expense of introducing a considerable uncertainty, we shall assume that to be the case. With this assumption Eq. (15) reduces to $\Delta H_a = -18.4RT$ for a 1-mole% BaO deficiency, and to $-16.1RT$ for a 0.1-mole% BaO deficiency, both for the case of $[V''_{Ba}] = [V_0^{\cdot\cdot}] =$ 10 ppm. The calculated values of $-\Delta H_a$ then range from 2.3 eV for the worst case of 1200°C and 1-mole% BaO deficiency to 1.5 eV for 800°C and 0·1-mole% BaO deficiency. Of course, the presence of oxygen vacancies related to the acceptor impurity will suppress dissociation to some extent. For the case of 1-mole% deficiency in BaO, $[V_0^{\cdot\cdot}] = 100$ ppm would reduce the absolute value of the calculated values of ΔH_a by about 15%. Moreover, the values will be even smaller if the entropy term favors association, which is not unlikely. Thus the values of $-\Delta H_a$ in the region of 2 eV would be adequate to fit the proposed model. On the other hand, association between $V_0^{\cdot\cdot}$ and the singly charged acceptor centers assumed to be present should be much less from simple coulombic considerations, and has been neglected.

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References

1. H. Veith, *Z. Angew. Phys.* **20**, 16 (1965).
2. F. Kosek and H. Arend, *Phys. Status Solidi* **24**, K69 (1967).
3. S. A. Long and R. N. Blumenthal, *J. Amer. Ceram. Soc.* **54**, 515 (1971).
4. S. A. Long and R. N. Blumenthal, *J. Amer. Ceram. Soc.* **54**, 577 (1971).
5. A. M. J. H. Seuter, *Philips Res. Rep. Suppl.*, No. 3 (1974).
6. N.-H. Chan and D. M. Smyth, *J. Electrochem. Soc.* **123**, 1585 (1976).
7. S. Ikegami and J. Ueda, *J. Phys. Soc. Japan* **19**, 159 (1964).
8. T. Murakami, T. Miyashita, M. Nakahara, and E. Sekine, *J. Amer. Ceram. Soc.* **56**, 294 (1973).
9. L. C. Walters and R. E. Grace, *J. Phys. Chem. Solids* **28**, 239 (1967).
10. W. L. George and R. E. Grace, *J. Phys. Chem. Solids* **30**, 881 (1969).
11. G. A. Cox and R. H. Tredgold, *Br. J. Appl. Phys.* **18**, 37 (1967).
12. A. Linz, V. Belruss, and C. S. Naiman, *J. Electrochem. Soc.* **112**, 60C (1965).
13. S. H. Wemple, M. Didomenico, Jr., and I. Camlibel, *J. Phys. Chem. Solids* **29**, 1797 (1968).
14. N. G. Eror and J. B. Wagner, Jr., *J. Phys. Chem. Solids* **29**, 1597 (1968).
15. H. Yamada and G. R. Miller, *J. Solid State Chem.* **6**, 169 (1973).
16. D. E. Rase and R. Roy, *J. Amer. Ceram. Soc.* **38**, 102 (1955).
17. H. Anderson, *J. Amer. Ceram. Soc.* **56**, 605 (1973).
18. N. G. Eror and D. M. Smyth, *in* "The Chemistry of Extended Defects in Non-Metallic Solids" (L. Eyring and M. O'Keeffe, Eds,), North–Holland, Amsterdam (1970).
19. R. J. Panlener and R. N. Blumenthal, *J. Amer. Ceram. Soc.* **54**, 610 (1971).
20. H. Arend and L. Kihlborg, *J. Amer. Ceram. Soc.* **52**, 63 (1969).
21. M. Didomenico, Jr., and S. H. Wemple, *Phys. Rev.* **166**, 565 (1968).
22. P. Kofstad, "Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides," Chaps. 11–12, Wiley Interscience, New York (1972).
23. G. J. Conger and H. U. Anderson, *J. Amer. Ceram. Soc.* **55**, 539 (1972).
24. F. A. Kröger, "Chemistry of Imperfect Crystals," Chaps. 9, 12, 15, 16, North–Holland, Amsterdam (1964).