



Comments on the Defect Chemistry of Undoped and Acceptor-Doped BaTiO₃

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Abstract. In a recent study of the defect chemistry of undoped polycrystalline and acceptor-doped single crystalline BaTiO₃, an attempt was made to obtain defect and thermodynamic parameters without any *a priori* assumptions, e.g. about the magnitude and temperature dependence of the carrier mobilities. The parameters found for the undoped sample differ significantly from those obtained from the acceptor-doped sample, and even more substantially from those reported from several earlier studies. It is suggested that these discrepancies result from the lack of sufficient data in certain critical regions of temperature and oxygen activity. As a result, the attempt to extract parameters from the equilibrium conductivity by multiparameter curve-fitting has considerable uncertainty. However, the electron and hole mobility products and ratios, $\mu_n\mu_p$ and μ_n/μ_p , were determined by linear extrapolation of the well-established log-log slopes of +1/4 and -1/4 for the equilibrium conductivities and oxygen diffusivities to their intersection. Both the products and the ratios were found to be independent of temperature, indicating that both mobilities are also independent of temperature. This important conclusion validates the thermodynamic parameters obtained in earlier studies in which it was assumed that the mobilities are temperature independent or nearly so, and that the carrier concentrations are proportional to the conductivities.

Keywords: BaTiO₃, defect chemistry, acceptor, equilibrium conductivity, enthalpy

1. Introduction

Yoo, Song, and Lee (YSL) have recently revisited the defect chemistry of undoped and acceptor-doped BaTiO₃ and have reported their analysis in this journal [1]. Their admirable goal was to obtain enough experimental data under equilibrium conditions so that the mass-action constants and their enthalpies, and the various defect concentrations could be obtained without any *a priori* assumptions. As they point out, much of the earlier work has been based primarily on analysis of the equilibrium electrical conductivity with assumptions about the electron and hole mobilities, particularly that they have little or no temperature dependence over the usual experimental range. However, YSL found quite different values for some parameters when results for undoped, polycrystalline BaTiO₃ and a 1.8% Al-doped single crystal were compared, even for parameters that are normally expected to be independent of the dopant concentration. While the results obtained

for the acceptor-doped sample differ somewhat from previously reported values, they are at least similar. However, results from the undoped sample differ significantly from those published previously. Some of these discrepancies are as follows:

1. The apparent background concentration of acceptor centers in the undoped sample was found to be thermally activated with an activation energy of 1.5 eV. No such temperature dependence has been previously reported.
2. The activation energy of ionic conductivity was also found to be 1.5 eV. Since this is the same value as that found for the extrinsic oxygen vacancy concentration, that implies that the mobility of oxygen vacancies is also independent of temperature.
3. The enthalpy of oxidation (the filling of extrinsic oxygen vacancies) was calculated from the enthalpy of reduction and the band gap. This gave a value of -1.0 eV for the undoped sample, while the temperature dependence of the *p*-type conduction indicates

a positive enthalpy. Others have found values in the +0.9–1.3 eV range [2–4].

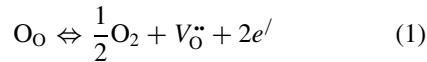
4. The presence of trapped holes was not taken into account by YSL. It has been previously reported that the holes generated by the oxidation reaction are mostly trapped, even at the equilibration temperatures [5–7].
5. The equilibrium constants for intrinsic electronic disorder (ionization across the band gap) obtained from two different sets of data obtained by YSL for the undoped sample differed by more than two orders of magnitude.
6. When the oxygen activities for the condition $\sigma_n = \sigma_p$ (the electron and hole conductivities) were calculated from two different kinds of data for the undoped sample, the agreement was very poor.

The mathematical analysis used by YSL appears to be valid. Thus it is of interest to determine why their results differ so much from those obtained by earlier investigators.

2. Background

Most of those who have investigated undoped and acceptor-doped BaTiO₃ (and SrTiO₃) agree that the important defects at the equilibration temperatures are the acceptor centers, A' , whether deliberately added or due to naturally-occurring impurities, doubly-ionized oxygen vacancies, $V_{\text{O}}^{\bullet\bullet}$, electrons, e' , and holes, h^{\bullet} . It is also possible that Schottky disorder, quenched in from the processing conditions, might contribute to the background acceptor content [8, 9]. More recently, holes trapped by the acceptor centers, A^x , have been added to the mix [5–7], such that the concentration hierarchy is $[A'] > [A^x] > p$, where $p = [h^{\bullet}]$. The equilibrium reactions and their mass-action expressions are:

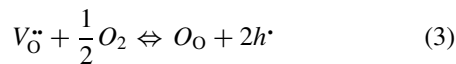
Reduction:



$$K_{\text{Re}} = [V_{\text{O}}^{\bullet\bullet}]n^2 P(\text{O}_2)^{\frac{1}{2}} \quad (2)$$

where $n = [e']$

Oxidation:



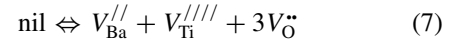
$$K_{\text{ox}} = \frac{p^2}{[V_{\text{O}}^{\bullet\bullet}]} P(\text{O}_2)^{-\frac{1}{2}} \quad (4)$$

Intrinsic electronic disorder:



$$K_i = np \quad (6)$$

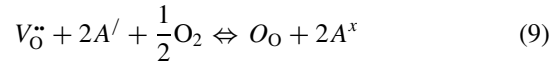
Schottky disorder



$$K_S = [V_{\text{Ba}}^{\prime\prime}][V_{\text{Ti}}^{\prime\prime\prime}][V_{\text{O}}^{\bullet\bullet}]^3 \quad (8)$$

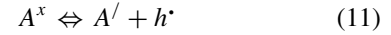
“nil” refers to the defect-free standard state. The importance of Schottky disorder is not entirely clear.

More recently, the oxidation reaction to form trapped holes has been added



$$K_{\text{Ap}} = \left(\frac{[A^x]}{[A']} \right)^2 \frac{1}{[V_{\text{O}}^{\bullet\bullet}]P(\text{O}_2)^{1/2}} \quad (10)$$

where A^x is an acceptor center with a trapped hole. Equations (3) and (9) are linked by the ionization reaction for trapped holes.



$$K_A = \frac{[A']}{[A^x]} p \quad (12)$$

Trapped holes, Eqs. (9)–(12), were not considered by YSL. Finally, there is the expression for bulk charge neutrality

$$n + [A'] = p + 2[V_{\text{O}}^{\bullet\bullet}] \quad (13)$$

It will be assumed that cation vacancies are either not a major defect or are quenched-in and temperature independent for the undoped and acceptor-doped materials. The n -type behavior of undoped and acceptor-doped BaTiO₃ can be divided into two limiting approximations to charge neutrality

$$\text{For high } P(\text{O}_2) \quad 2[V_{\text{O}}^{\bullet\bullet}] = [A'] \quad (14)$$

$$\text{For very low } P(\text{O}_2) \quad 2[V_{\text{O}}^{\bullet\bullet}] = n \quad (15)$$

Simultaneous solution of these relationships leads to the classic Kröger-Vink type of diagram shown in

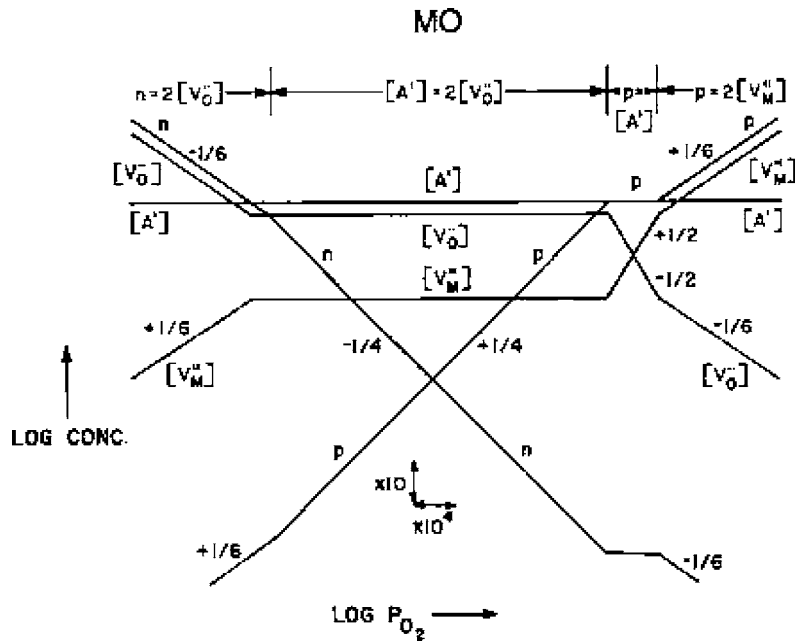


Fig. 1. A Kröger-Vink diagram for a hypothetical acceptor-doped oxide, MO, in which the mass-action constant for Schottky disorder exceeds that of intrinsic electronic disorder by a factor of 10^6 . The oxygen vacancy concentration has been increased by a factor of ten over the intrinsic level as a result of the added acceptor content. Adapted from Fig. 3 in [16].

Fig. 1, which is a log-log plot of defect concentrations against oxygen activity at constant temperature under conditions of oxygen equilibrium. It is assumed that the temperature dependences arise from a characteristic enthalpy, ΔH , for each of the mass-action constants, which take the form

$$K_j = K_j^o \exp\left(-\frac{\Delta H_j}{kT}\right) \quad (16)$$

A quantitative defect model involves the determination of all of the mass-action constants and their enthalpies, and the concentrations of the various defect species as a function of temperature, oxygen activity, and dopant concentration.

3. The Equilibrium Conductivity

YSL measured the equilibrium conductivity of undoped and acceptor-doped BaTiO₃ as a function of oxygen activity at 800, 900, 1000, and 1100°C [1]. Their results for the undoped, polycrystalline sample are shown in Fig. 2. As shown in their paper, their data are very similar to those obtained by several other groups. In the region where Eq. (14) is valid, the log-

log slopes are $+1/4$ (*p*-type) and $-1/4$ (*n*-type), which must be separated by a minimum in the conductivity. Under the most reducing conditions, Eq. (15) becomes the approximation to charge neutrality and the log-log

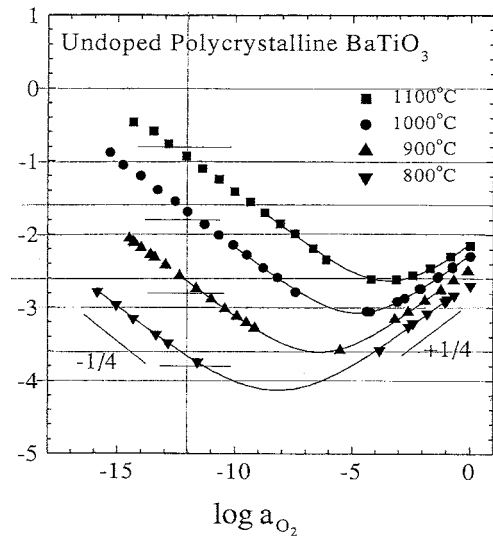


Fig. 2. The equilibrium conductivity of undoped BaTiO₃ as measured by YSL and used by them to derive the values of the defect concentrations and reaction enthalpies [1].

slope has been shown to change to the expected value of $-1/6$.

The conductivity is primarily electronic but there is a detectable ionic contribution from the oxygen vacancies that compensate for the charge of the acceptor content. Where Eq. (14) is valid, the oxygen vacancy concentration, and its contribution to the total conductivity, should be nearly independent of the oxygen activity. The ionic component is then most apparent near the conductivity minima. It is possible to obtain the ionic conductivity by deconvoluting the curvature of the conductivity data near the minima [2, 10]. Another critical point is the intersection of the regions with log-log slopes of $-1/4$ and $-1/6$. This occurs where the electron concentration equals the acceptor concentration, and can be used to determine the latter if the electron mobility is known.

4. The Ionic Conductivity

While the ionic conductivity is a relatively minor component of the equilibrium electrical conductivity of undoped BaTiO_3 , its value and temperature dependence are crucial to the defect analysis offered by YSL, because it appears in the derivations of several other parameters. The only information in the equilibrium conductivity on the magnitude of the ionic component is in the deviation of the total conductivity from the sum of the ideal electronic components due to electrons and holes. This deviation is most apparent for the range of oxygen activities near the conductivity minima.

YSL derive an expression for the total equilibrium conductivity in the region where Eq. (14) is valid by combination of Eqs. (2), (6), and (14).

$$\sigma = \sigma_{\text{el},m} \cosh \left[\frac{1}{4} \ln \frac{a(\text{O}_2)}{a(\text{O}_2)^*} \right] + \sigma_{\text{ion}} \quad (17)$$

(We shall now use the form $a(\text{O}_2)$, rather than $P(\text{O}_2)$, in order to correspond to the convention used by YSL.) The first term on the right-hand-side is the contribution by electrons and holes. $\sigma_{\text{el},m}$ is the total electronic conductivity at the conductivity minimum, $a(\text{O}_2)$ is the oxygen activity, and $a(\text{O}_2)^*$ is the oxygen activity at the minimum. This equation was then fit to the data at each temperature in Fig. 2 by a nonlinear-least-squares (NLLS) technique; the fit is indicated by the solid lines in that figure. This process yielded values of $\sigma_{\text{el},m}$, $a(\text{O}_2)^*$, and σ_{ion} as fitting parameters.

YSL found that the ionic conductivity is thermally activated with an activation energy of 1.52 eV for the undoped, polycrystalline sample and 0.84 eV for the 1.8% Al-doped single crystal. These values not only differ from each other; they are not very close to the range of values, 1.0–1.1 eV, found by other investigators for BaTiO_3 , SrTiO_3 , and other similar perovskites [2, 11]. No such dependence of the activation energy on the acceptor concentration has been previously noted. Using more complete sets of data of this type, we have previously determined the ionic conductivity of undoped and acceptor-doped BaTiO_3 by three different techniques [2, 10]. In one case, the extrapolated electronic conductivity at the minimum was subtracted from the total measured conductivity at the minimum [2]. This gave an activation energy for the ionic component of 1.1 eV for both undoped samples and for samples with added acceptor concentrations up to 0.15% (% substitution on the B-sites), and a value of $\log \sigma_{\text{ion}}$ for the undoped material at 1000°C of -3.96 . The second technique involved deconvoluting the curvature on either side of the minima by use of the following approximations [10]

$$\sigma_t = \sigma_{\text{ion}} + \sigma_p^o a(\text{O}_2)^{1/4} \quad (18)$$

where σ_t is the total, measured conductivity and σ_p^o is the p -type conductivity at $a(\text{O}_2) = 1$ atm. This is a good approximation for oxygen activities greater than that at the minimum such that $\sigma_p > \sigma_n$. For oxygen activities below that at the minimum, such that $\sigma_n > \sigma_p$, the approximation is

$$\sigma_t = \sigma_{\text{ion}} + \sigma_n^o a(\text{O}_2)^{-1/4} \quad (19)$$

where σ_n^o is the n -type conductivity at $a(\text{O}_2) = 1$ atm. Thus plots of the total, measured conductivity in the appropriate regions against $a(\text{O}_2)^{1/4}$ and $a(\text{O}_2)^{-1/4}$ give straight lines with the same intercept, which is σ_{ion} , as shown in Fig. 3. This gave a value of $\log \sigma_{\text{ion}}$ for undoped BaTiO_3 at 1000°C of -4.05 , in excellent agreement with the value found by the first technique as quoted above. It was found that the ionic transport numbers derived from these measurements are in excellent agreement with those obtained from oxygen concentration cells, the third technique [10]. Thus the absolute value of the ionic conductivity and the ionic transport numbers can both be derived from just the measured equilibrium conductivity as a function of oxygen activity. Why do the results of YSL differ so much from these earlier results?

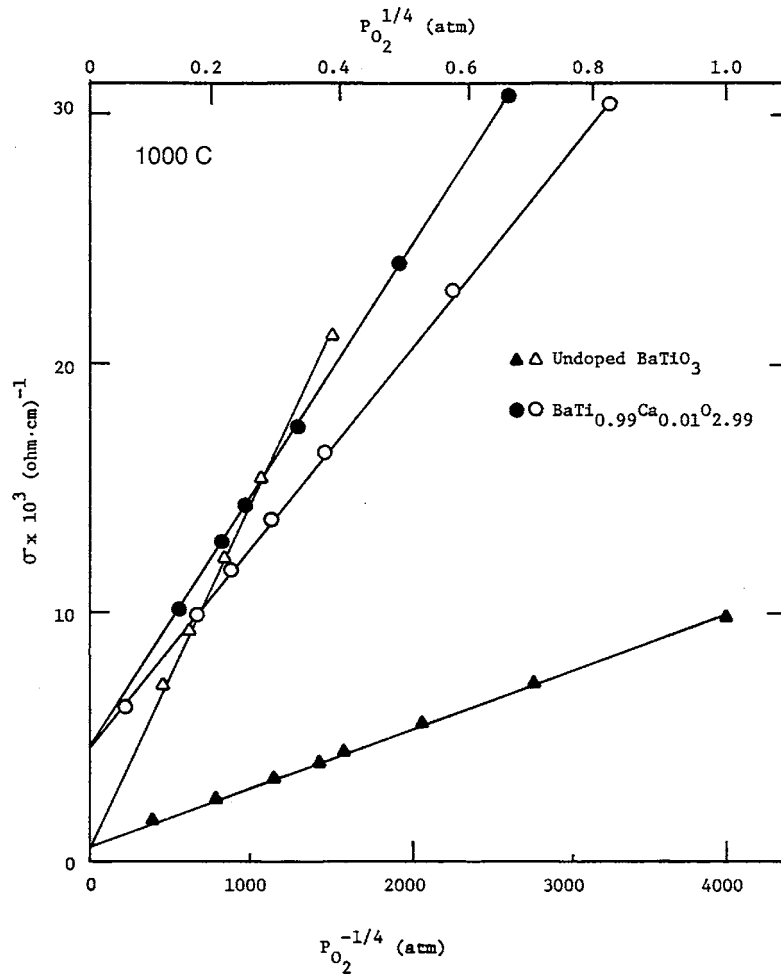


Fig. 3. The total equilibrium conductivity of undoped and 1% acceptor-doped BaTiO₃ at 1000°C plotted according to Eqs. (18) and (19). The solid symbols refer to the *p*-type side, Eq. (18), and the upper abscissa, while the open symbols refer to the *n*-type side, Eq. (19), and the lower abscissa. The ionic conductivity is given by the intercepts to the ordinate. Adapted from Fig. 4 of [6].

YSL present sufficient data to establish quite accurately the log-log slopes of +1/4 and -1/4 on either side of the minima. Since $\sigma_{el,m}$ and $a(O_2)^*$ are determined by linear extrapolation of these log-log slopes to their intersection point, these parameters can be obtained with considerable accuracy. However, σ_{ion} will depend on an accurate determination of the total conductivity near the minimum. Unfortunately, the experimental data of YSL show the commonly observed data gap between the regions of high and low oxygen activities. Thus there are very little data in the most critical region for the determination of the ionic component. This gap arises from the use of metered gas flows to determine the oxygen activities. At high activities pure oxygen is

gradually diluted with argon. As the ratio of the flow rates drops to 1:10⁴ or 1:10⁵, it becomes increasingly difficult and eventually impossible to measure the flow rate of the more dilute gas accurately. Similarly, in the mixtures of CO and CO₂ used to fix the oxygen activities at very low values, the flow rate of CO eventually becomes too small to measure. The result is a data gap between the lowest O₂ flow rate in Ar, and the lowest flow rate of CO in CO₂. As shown in Fig. 2, this gap becomes wider with decreasing equilibration temperatures. At 800°C, the data of YSL show a gap of 8 orders of magnitude, with the conductivity minimum approximately in the center. The deviation from the ideal electronic slopes of +1/4 and -1/4 increases

toward the minimum, so the most important information is found in the last data points adjacent to the gap. The data of YSL show almost no such deviation, and the last data point at the high activity boundary of the gap at 800°C actually deviates in the wrong direction. The same is true of the last data points at the low activity boundary of the gaps at 1000 and 1100°C. The inaccuracies of these most important data points must result in considerable uncertainty in the extrapolated shape of the conductivity minima and the resulting value of the ionic conductivity. In general, the data give very little guidance for the curve-fitting which is trying to find the correct path for the conductivity across the wide gap. As a result, whenever the determination of the precise curvature near the minimum enters into the derivation of a defect parameter, the values derived from the 800°C data deviate from the Arrhenius slope established by the data at the three higher temperatures and are discarded from the analysis. The ionic contribution to the total equilibrium conductivity decreases with increasing temperature, since the minimum electronic conductivity is rising faster than the ionic component. Thus the data at the lower temperatures are the most valuable. As shown in Fig. 4, techniques have been developed that make it possible to obtain conductivity data across the gap [2, 12]. These involve the use of electrochemical

oxygen pumps and leaks based on the oxygen conductivity of acceptor-doped zirconia, and the use of the same material as an electrochemical oxygen activity sensor. It was these types of data that were used to determine the ionic conductivity as described above. It is probable that the type of curve-fitting attempted by YSL would have been much more successful if it had been applied to such a complete set of data.

Curve-fitting the equilibrium conductivity data for the 1.8% acceptor-doped single crystal seems to have been more successful. First of all, there are more data points in the critical areas adjacent to the gaps, and the points adjacent to the gaps appear to fall nicely on the fitted curve. The ionic conductivity of this sample should be much higher than that of the undoped sample. Thus much more curvature is apparent near the gaps and this enhances the accuracy of the curve-fitting. The data obtained at 800°C are not anomalous, and the resulting activation energy for ionic conduction is much closer to previously reported values. This carries through to the other parameters derived for the acceptor-doped sample, which are mostly similar to those obtained from earlier studies, whereas for the undoped sample the agreement is poor. It is proposed that the results of the analysis of the equilibrium conductivity of the undoped sample are strongly affected

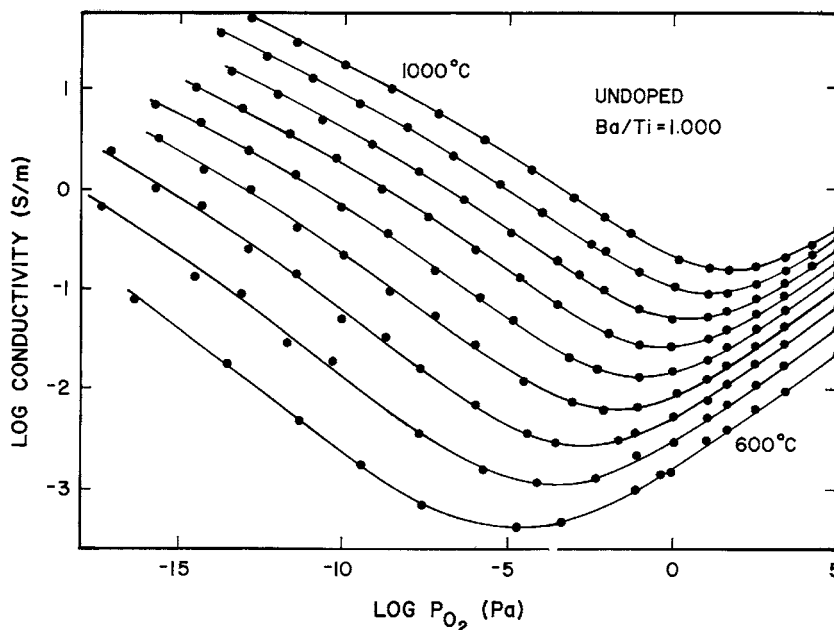


Fig. 4. The equilibrium conductivity of undoped BaTiO_3 as a function of oxygen activity as obtained in our laboratory. The isotherms are at intervals of 50°C.

by the absence of sufficient data in the most critical regions.

So far, all of the analysis has involved only conductivities, and it has not been necessary to make any assumptions about the electron and hole mobilities.

5. The Defect Parameters

The following parameters were obtained by YSL by a mathematical fit to their total conductivity isotherms: σ_n , σ_p , σ_{ion} , $\sigma_{\text{el},m}$, and $a(\text{O}_2)^*$ (the oxygen activity where $\sigma_n = \sigma_p$).

The authors also measured the chemical diffusivity of oxygen as a function of oxygen activity at the same four temperatures by means of a conductivity relaxation technique. There are sufficient diffusion data at high and low oxygen activities to extrapolate the positive and negative slopes, respectively, to their intersection point. This allowed the accurate determination of $a(\text{O}_2)^o$, the oxygen activity where $n = p$. They then state "By combining these pieces of information, one can evaluate the defect parameters without using any ad hoc assumptions regarding, e.g., the densities of states and carrier mobilities, contrary to the previous works." Their results are compared with those of earlier investigations in Table 1.

ΔH_μ is the activation energy for the electron and hole mobilities. The values of the various parameters for the acceptor-doped single crystal are in the vicinity of those reported previously, while those for the undoped polycrystalline sample deviate substantially, with the exception of the band gap and the temperature dependence of the electron and hole mobilities.

The band gap, E_g^o , for the undoped sample was obtained from the temperature dependence of the mass-action constant for intrinsic electronic disorder, Eq. (6).

Table 1. Comparison of defect parameters obtained by YSL, Ref. [1], with those reported previously

Parameter	YSL undoped	YSL, acceptor-doped	Previously reported
E_g^o	3.15 eV	–	2.9–3.4 eV
ΔH_{Re}	7.3	5.88	5.7–6.1
ΔH_{ox}	–1.0	+0.42	+0.8–1.3
$[A']$	1.52	0	~0
σ_{ion}	1.52	0.84	1.0–1.1
ΔH_μ	~0	–	small or 0

The latter was obtained by fitting the diffusivity data according to the relationship

$$K_i = \left(\frac{kT\sigma_{\text{ion}}t_e}{2e^2\tilde{D}} \right)^2 \cosh^{-2} \left[\frac{1}{4} \ln \frac{a(\text{O}_2)}{a(\text{O}_2)^o} \right] \quad (20)$$

with the fitting parameters K_i and $a(\text{O}_2)^o$, using the derived values for σ_{ion} and t_{el} , and the experimental values for \tilde{D} , the diffusivity. This analysis gave a band gap of 3.15 eV, in quite good agreement with previously determined values. Once again the value of K_i at 800°C was anomalous and was disregarded. K_i can also be determined, more directly, from the relationship

$$\frac{K_i}{\mu_n\mu_p} = \frac{\sigma_{\text{el},m}^2}{4e^2} \quad (21)$$

While the mobility product $\mu_n\mu_p$ is as yet unknown, an Arrhenius plot of $K_i/(\mu_n\mu_p)$ gave a slope of 3.25 eV which agrees quite well with the value derived from Eq. (20), and is in even better agreement with values obtained by other investigators. This indicates that the mobility product is quite insensitive to temperature, a very important point. The mobility ratio, μ_n/μ_p can be obtained from

$$\frac{\mu_n}{\mu_p} = \left[\frac{a(\text{O}_2)^*}{a(\text{O}_2)^o} \right]^{1/2} \quad (22)$$

The ratio thus depends on the separation between $a(\text{O}_2)^*$, the oxygen activity where $\sigma_n = \sigma_p$ as obtained from the conductivity data, and $a(\text{O}_2)^o$, the oxygen activity where $n = p$ as determined from the diffusivity data. The mobility ratio turns out to be temperature independent, and since the mobility product is also temperature independent, the electron and hole mobilities must each be temperature independent (if the value at 800°C is neglected). The values determined by YSL for the temperature range 900–1100°C are

$$\begin{aligned} \mu_n &= 0.13 \text{ cm}^2/\text{v}\cdot\text{sec} \\ \mu_p &= 0.08 \end{aligned} \quad (23)$$

These values are close to those determined for single crystal $\text{Ba}_{0.03}\text{Sr}_{0.97}\text{TiO}_3$ by Choi, Tuller, and Goldschmidt, who also found them to be temperature independent [13]. Thus the earlier intuitive guess that the hole mobility should be about one half of the electron mobility has proven to be quite close to reality [2, 12].

The electron and hole concentrations, n and p , can now be obtained from the conductivity and the mobilities just determined. Then the mass-action constant for the reduction reaction, K_{Re} [Eqs. (1) and (2)], and the apparent acceptor concentration, $[A']$, can be obtained from the expression

$$a(\text{O}_2)^{1/2} = \frac{2K_{\text{Re}}}{n^2} \left(n + [A'] + \frac{K_i}{n} \right)^{-1} \quad (24)$$

Since $[A']$ and K_{Re} are both fitting parameters for Eq. (24), their values are linked. For the undoped sample, K_{Re} was found to be thermally activated with an enthalpy of 7.3 eV, which is substantially higher than previously reported values, as shown in Table 1. The acceptor concentration was also found to be thermally activated with an activation energy of 1.52 eV. In both cases the results at 800°C were excluded. No such temperature dependence for the acceptor concentration has been found previously. For the acceptor-doped single crystal the enthalpy of reduction was found to be 5.88 eV and the acceptor content was independent of temperature, both in excellent agreement with previous reports. So why are the results for the undoped sample so different? It is suggested that once again the problem is related to the lack of data in a critical region.

The acceptor concentration is equal to the electron concentration at the point where the log-log slopes of $-1/4$ and $-1/6$ intersect. The conductivity data for the undoped sample cut off at oxygen activities of about 10^{-14} – 10^{-16} atm, and there is little evidence of the region with slope $-1/6$, particularly at the lower temperatures, since the intersection point moves rapidly to lower oxygen activities with decreasing temperature. Moreover, the change in slope defined by the last two data points at 1100°C is much more abrupt than expected. The ideal transition between the two slopes has been shown to be much more gradual [7]. As shown in Fig. 4, some of the earlier data extend to lower oxygen activities by five or six orders of magnitude, and therefore contain more information about the intersection point. Thus it is suggested that the apparent thermal activation of the acceptor results from insufficient data, and is incorrect. If the apparent acceptor content is thermally activated, then the compensating oxygen vacancies must also be thermally activated with the same activation energy, 1.52 eV. But the ionic conductivity also appeared to have an activation energy of 1.52 eV, which means that the vacancy mobility would have to be independent of temperature, which would conflict

with all previous work, as well as the normal expectation for an ionic mobility.

The more fundamental point would be that the extrinsic oxygen vacancy concentration is thermally activated, since it is $[V_{\text{O}}^{\bullet\bullet}]$ that appears in the mass-action expression, Eq. (2). For the model used by YSL, as exemplified by the approximation to charge neutrality shown in Eq. (14), the oxygen vacancy and acceptor concentrations are linked so that the latter also appears to be thermally activated. It will be shown later that there are cases where the extrinsic oxygen vacancy concentration can be thermally activated even when the total acceptor concentration is independent of temperature.

If one makes an Arrhenius plot of the conductivity data of YSL at an oxygen activity of 10^{-12} atm, the slope is 2.65 eV, which indicates an enthalpy of reduction, K_{Re} , of 5.3 eV, much closer to generally accepted values. This should be a true enthalpy since YSL have determined that the electron mobility is temperature independent. Also, the conductivity at 800°C falls right on the linear Arrhenius plot. This indicates that there is no problem with the data measured at 800°C; the problem is in trying to extrapolate the conductivity across the data gap. Let us assume that the true value of the apparent enthalpy just derived is that determined for the acceptor-doped single crystal, 5.9 eV, in agreement with previously reported values. (The value of 5.3 eV reported above depends on our rather crude attempt to read the conductivities from Fig. 2.) The only way for the activation enthalpy in the impurity-controlled region to be 5.9 eV, while the true enthalpy of reduction is 7.3 eV, is for the apparent acceptor content to also be thermally activated. For the latter to be true, Eq. (14) can no longer be used as a temperature-independent approximation to charge neutrality and must be replaced by

$$[A'] = [A']^o \exp\left(\frac{-\Delta H_a}{kT}\right) = 2[V_{\text{O}}^{\bullet\bullet}] \quad (25)$$

where ΔH_a is the activation energy for the apparent acceptor content. When this value of $[V_{\text{O}}^{\bullet\bullet}]$ is substituted into Eq. (2), the mass-action expression for the reduction reaction, expanded to show the enthalpy term, one gets

$$n = \left(\frac{2K_{\text{Re}}^o}{[A']^o} \right)^{1/2} a(\text{O}_2)^{-1/4} \exp\left(-\frac{\Delta H_{\text{Re}} - \Delta H_a}{2kT}\right) \quad (26)$$

We have just determined that $\Delta H_{\text{Re}} - \Delta H_a = 5.9$ eV, so if $\Delta H_a = 1.5$ eV, then ΔH_{Re} is 7.4 eV, as proposed by YSL. The latter authors point out this relationship but its origin was not clear. If the acceptor concentration, and hence the extrinsic oxygen vacancy concentration, is thermally activated, the enthalpy of the reduction reaction must be larger than the activation enthalpy found in the acceptor-controlled region. The difference will be the enthalpy of activation of the acceptor content. This interdependence results from the linkage between the apparent acceptor concentration and the mass-action constant for the reduction reaction, since they are both fitting parameters for Eq. (24). It is also required by the simple plane geometry of the corresponding Kröger-Vink diagrams. If the acceptor content is temperature independent, as found by all other groups, then the true value of ΔH_{Re} is 5.9 eV.

YSL obtained the enthalpy of the oxidation reaction by using the relationship [5]

$$K_{\text{ox}} = \frac{K_i^2}{K_{\text{Re}}} \quad (27)$$

which indicates that

$$\Delta H_{\text{ox}} = 2E_g^o - \Delta H_{\text{Re}} \quad (28)$$

This resulted in a negative value for ΔH_{ox} , -1.00 eV, for the undoped sample which is counter to the observed sign of the temperature dependence of the p -type equilibrium conductivity (Fig. 2). Since YSL show that the hole mobility is independent of temperature, the temperature dependence of the conductivity accurately represents the temperature dependence of the hole concentration, and ΔH_{ox} must be positive. Equations (27) and (28) are valid only for the case that the acceptor content is independent of temperature, and cannot be used for the defect model proposed for the undoped sample by YSL. These relationships are valid for their model for the acceptor-doped single crystal, where the acceptor content is not activated. Thus they obtain an oxidation enthalpy of $+0.42$ eV for the latter sample, smaller than found previously, but at least a positive value. If ΔH_{Re} for the undoped sample is taken to be 5.9 eV instead of 7.3 eV, then ΔH_{ox} would also be $+0.4$ eV. Equation (28) has previously been found to be in excellent agreement with experimental results [2, 5, 7], which indicates that the acceptor content is not thermally activated.

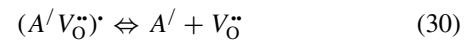
6. An Activated Acceptor Content?

What could result in a thermally activated acceptor content? While this author believes that the thermal activation reported by YSL is an artifact due to a lack of critical data, it is interesting to speculate about a specific model, and to see how it affects the analysis. Three possibilities come to mind. The first would require that the acceptor content be in excess of the solubility limit so that there is a reservoir of acceptors in the grain boundaries. This would require that the solubility limit for all of the acceptors present be exceedingly low, and that they be able to diffuse in and out of the lattice over the entire experimental temperature range. However, the fact that samples can be prepared with acceptor concentrations in excess of 1%, e.g. the 1.8% acceptor-doped single crystal used by YSL, makes this possibility extremely unlikely. Another possibility is that intrinsic Schottky disorder be able to stay in equilibrium over the entire temperature range. Since reproducible equilibrium conductivities have been measured down to 600°C, this also seems unlikely. Finally, the acceptors could be strongly attached to the compensating oxygen vacancies in the form of defect complexes. While there is no evidence for a significant concentration of such complexes under equilibration conditions, this model will be used to explore the consequences of a thermally activated acceptor content. For the sake of simplicity, we will ignore the trapping of holes by the acceptor centers. Since this results in an uncharged species, the effect on the other equilibrium defect concentrations is negligible.

It will be assumed that almost all of the compensating oxygen vacancies are attached to an acceptor center in the form $(A^{\prime}V_{\text{O}}^{\bullet\bullet})^{\bullet}$. Since there will be only half as many extrinsic oxygen vacancies as singly-charged acceptor centers, there will then be nearly equal numbers of acceptors in complexes and free acceptors

$$[A^{\prime}] = [(A^{\prime}V_{\text{O}}^{\bullet\bullet})^{\bullet}] \quad (29)$$

To the usual set of equilibrium relationships represented by Eqs. (1)–(6), we will add the dissociation reaction for the complexes



$$\frac{[A^{\prime}][V_{\text{O}}^{\bullet\bullet}]}{[(A^{\prime}V_{\text{O}}^{\bullet\bullet})^{\bullet}]} = K_D^o \exp\left(-\frac{\Delta H_D}{kT}\right) \quad (31)$$

It will be assumed that the change in oxygen content is small compared with the concentrations of complexes and free acceptors. Thus Eq. (29) can serve as the approximation to charge neutrality over most of the impurity-controlled region. Combination of Eqs. (29) and (31) gives

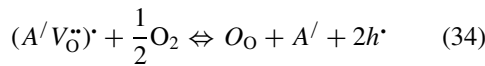
$$[V_{\text{O}}^{\bullet}] = K_D^o \exp\left(-\frac{\Delta H_D}{kT}\right) \quad (32)$$

This gives a thermally-activated concentration of unbound oxygen vacancies as suggested by YSL. It should also be noted that this is a case where the free vacancy concentration is thermally activated while the total acceptor content remains temperature independent. The concentration of compensating oxygen vacancies is invariant with the oxygen activity in this region. As vacancies are created or consumed as the oxygen activity decreases or increases, the complex increases or dissociates to the small extent necessary to maintain the constant vacancy concentration specified by Eq. (32). When Eq. (32) is substituted for the extrinsic oxygen vacancy concentration in the mass-action expression for the reduction reaction, Eq. (2), expanded according to Eq. (16) to show the enthalpy of reduction, the electron concentration becomes

$$n = \left(\frac{K_{\text{Re}}^o}{K_D^o}\right)^{1/2} a(\text{O}_2)^{-1/4} \exp\left(-\frac{\Delta H_{\text{Re}} - \Delta H_D}{2kT}\right) \quad (33)$$

This is a more model-specific version of Eq. (26), and the discussion following that equation is also valid for this specific model. It shows that if the combined enthalpy term in the impurity-controlled region is 5.9 eV, then ΔH_{Re} must be 7.4 eV, as proposed by YSL.

Since the extrinsic oxygen vacancy concentration depends only on the temperature, the oxidation reaction is better described as the filling of the vacancies in the complex



with an enthalpy ΔH_{ox} . The relationships between the enthalpies can then be shown to be

$$\Delta H_{\text{Re}} - 2E_g^o = \Delta H_D - \Delta H_{\text{ox}} \quad (35)$$

since Eq. (1) minus twice the reverse of Eq. (5) equals Eq. (30) minus Eq. (34). Thus

$$\begin{aligned} \Delta H_{\text{ox}} &= 2E_g^o + \Delta H_D - \Delta H_{\text{Re}} = 6.5 + 1.5 - 7.3 \\ &= +0.7\text{eV} \end{aligned} \quad (36)$$

This is close to the usually determined experimental values near +1 eV [2–4] and is in accord with the observed increase of the *p*-type equilibrium conductivity with temperature. The negative value for ΔH_{ox} proposed by YSL resulted from the absence of ΔH_D in their version of Eq. (35).

This hypothetical model of complex formation between the acceptor centers and the oxygen vacancies is, however, inconsistent with the experimental data. In this model the free oxygen vacancy concentration is suppressed by complex formation and is liberated from the complexes with an activation energy of 1.52 eV. This will result in an increase in the free vacancy concentration by a factor of 36 as the temperature increases from 800 to 1100°C. Since there is no evidence of saturation, i.e. that a significant fraction of the remaining free acceptors have become complexed, it would appear that the free oxygen vacancy concentration has been suppressed below the total acceptor concentration by at least three orders of magnitude. As the electron concentration increases with reduction with a log-log slope of $-1/4$, it will rise above the free oxygen vacancy concentration, which is constrained by Eq. (32) to remain independent of the oxygen activity. The additional oxygen vacancies formed by reduction will be consumed by complex formation with the remaining free acceptors. However, when the electron concentration reaches the total acceptor concentration, essentially all of the acceptors will have been complexed. With further reduction, the free acceptor concentration will fall away with a log-log slope of $+1/2$, while the free oxygen vacancies rise with a slope of $-1/2$. The electron concentration is constrained to stay at the level of the complexed acceptors in order to maintain charge neutrality and the approximation to charge neutrality in this region is then

$$n = [(A'V_{\text{O}}^{\bullet})] \quad (37)$$

The width of this plateau in the electron concentration must be twice the number of orders of magnitude by which the free oxygen vacancy concentration was suppressed by the complex formation, in other

words, at least six orders of magnitude. When the free oxygen vacancy concentration finally reaches the total acceptor concentration, the n -type conductivity can then rise with the familiar $-1/6$ slope that is characteristic of intrinsic nonstoichiometry. No such plateau has been observed separating the transition between the log-log slopes of $-1/4$ and $-1/6$. In fact the conductivity data in this region have been successfully fit by several groups as a direct transition between the two slopes [2–4]. Thus any attempt to justify an apparent thermal activation of the extrinsic oxygen vacancy concentration as being due to complex formation with the acceptor centers is refuted by the experimental evidence.

7. The Carrier Mobilities

In order to translate conductivity data into carrier concentrations, the carrier mobilities must be known. In order to obtain reaction enthalpies only the temperature dependence of the mobilities is needed. One of the major goals of YSL was to obtain mass-action constants and reaction enthalpies for various defect reactions without making any assumptions about the carrier mobilities. The earlier investigators have generally assumed that the mobilities have either very little or no temperature dependence, such that enthalpies can be obtained directly from conductivity measurements. In our own early work, the Hall mobility obtained by Seuter was used for the electrons [7, 14, 15]. This work indicated a $T^{-3/2}$ dependence for the electron mobility which was factored into the treatment of the experimental data. No such information was available for the holes, and it was assumed that their mobilities have the same temperature dependence as the electrons. In any case, these temperature dependences had very little effect on the derived enthalpies.

Ironically, YSL have found that both the electron and hole mobilities have negligible temperature dependences, in agreement with earlier findings for $\text{Ba}_{0.03}\text{Sr}_{0.97}\text{TiO}_3$ [13]. This justifies the assumptions made in the earlier work and indicates that the enthalpies reported from those studies are reliable. It may seem perverse to question the validity of most of the results obtained by YSL for undoped BaTiO_3 , and then stress the importance of one specific finding. However, examination of the derivation of their mobilities suggests that these results are valid. YSL obtained the band gap from Arrhenius plots of the mass-action constants

for intrinsic electronic disorder, K_i . The latter values were obtained in two ways. The first approach involved a detailed relationship that involves the ionic conductivity, electronic transport number, and chemical diffusivity of oxygen, Eq. (20). This gave a band gap of 3.15 eV. The second approach involved Eq. (21) in which the only experimental value is the minimum electronic conductivity, $\sigma_{\text{el},m}$. The latter can be accurately obtained by extrapolation of the log-log slopes of $+1/4$ and $-1/4$ for the p -type and n -type conductivities to their point of intersection. This gave a band gap of 3.25 eV, in reasonable agreement with the value obtained by the other approach, and well within the range of previously reported values. Thus the band gap determined by YSL is accurate, and this implies, from Eq. (21) that the mobility product, $\mu_n\mu_p$, is temperature independent. The mobility ratio, μ_n/μ_p , can be obtained from the separation of $a(\text{O}_2)^*$, the oxygen activity at the conductivity minimum, from $a(\text{O}_2)^o$, the oxygen activity where $n = p$, according to Eq. (22). $a(\text{O}_2)^*$ can be accurately obtained by extrapolation of the log-log slopes of $+1/4$ and $-1/4$ for the p -type and n -type conductivities to their intersection, and $a(\text{O}_2)^o$ can be determined by extrapolation of the log-log slopes of $+1/4$ and $-1/4$ for the chemical diffusivity of oxygen in the p -type and n -type regions to their intersection. From these results, Eq. (22) shows that the mobility ratio is also temperature independent. If the product and the ratio are both temperature independent, then μ_n and μ_p must each be temperature independent. This detailed analysis is only possible because of the extensive set of chemical diffusivity data obtained by YSL. The important point is that the claim by YSL that both μ_n and μ_p are temperature independent is well-supported. This means that the thermodynamic parameters obtained by earlier investigators by a more direct analysis of the conductivity data are reliable. The only parameter that depends on detailed information about the curvature of the equilibrium conductivity near the minima is the ionic conductivity.

8. Summary

YSL have attempted to obtain an accurate, self-consistent set of defect parameters, i.e. mass-action constants, reaction enthalpies, and mobilities for BaTiO_3 by analysis of the equilibrium electrical conductivity, the deviations from stoichiometry, and the chemical diffusivity of oxygen. In principle this will

yield the desired parameters without any a priori assumptions about the carrier mobilities and their temperature dependences. Previous analyses have assumed that the mobilities have negligible temperature dependences so that the thermodynamic parameters can be obtained directly from the temperature dependence of the equilibrium conductivity. For absolute values, the Hall mobilities measured for electrons by Seuter have been used [2, 12, 14, 15].

The thermodynamic parameters obtained by the analysis of YSL differ markedly from those reported previously, particularly for the case of the undoped material. This is attributed to the lack of sufficient data in the most critical experimental regions such that the reliability of the curve-fitting is seriously impaired. In particular, accurate determination of the contribution made by ionic conduction is crucial in the derivation of the values of the other defect parameters. This contribution is evidenced only in the amount of curvature of the log-log plots of the equilibrium conductivity as a function of oxygen activity near the conductivity minima. That is precisely the region where the data are missing. It does appear that YSL are able to obtain valid values for the electron and hole mobilities. Both prove to be temperature independent. This supports the earlier approaches and indicates that the defect parameters can be accurately obtained from the temperature dependence of the equilibrium conductivity alone. It is

thus suggested that the true values are those given in the right-hand column of Table 1 above.

References

1. H.-I. Yoo, C.-R. Song, and D.-K. Lee, *J. Electroceramics*, **8**, 5 (2002).
2. N.-H. Chan, R.K. Sharma, and D.M. Smyth, *J. Am. Ceram. Soc.*, **65**, 167 (1982).
3. S.A. Long and R.N. Blumenthal, *J. Am. Ceram. Soc.*, **54**, 577 (1971).
4. G.M. Choi and H.L. Tuller, *J. Am. Ceram. Soc.*, **71**, 201 (1988).
5. R. Waser, *J. Am. Ceram. Soc.*, **74**, 1934 (1991).
6. M.V. Raymond and D.M. Smyth, *Integrated Ferroelectrics*, **4**, 145 (1994).
7. D.M. Smyth, *The Defect Chemistry of Metal Oxides* (Oxford University Press, New York, 2000), Chap. 14.
8. R. Moos and K.H. Hardtl, *J. Am. Ceram. Soc.*, **78**, 2569 (1995).
9. R. Moos and K.H. Hardtl, *J. Am. Ceram. Soc.*, **80**, 2549 (1997).
10. E.K. Chang, A. Mehta, and D.M. Smyth, in *Proceedings of a Symposium on Electro-Ceramics and Solid-State Devices*, edited by H.L. Tuller and D.M. Smyth (The Electrochem. Soc., Pennington, NJ, 1988), p. 35.
11. T. Takahashi, in *Physics of Electrolytics*, Vol. 2, edited by J. Hladik (Academic Press, New York, 1972), Chap. 24.
12. N.-H. Chan, R.K. Sharma, and D.M. Smyth, *J. Am. Ceram. Soc.*, **64**, 556 (1981).
13. G.M. Choi, H.L. Tuller, and D. Goldschmidt, *Phys. Rev. B*, **34**, 6972 (1986).
14. A.M.J.H. Seuter, *Philips Res. Rpt. Suppl.*, **3**, 1 (1974).
15. H. Irhig, *J. Phys. C*, **9**, 3469 (1976).
16. D.M. Smyth, *Prog. Solid St. Chem.*, **15**, 145 (1984).