Defect Structure, Nonstoichiometry and Nonstoichiometry Relaxation of Complex Oxides

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ABSTRACT

An SOFC consists of all ceramic complex oxides each with different electrochemical-property requirements. These requirements, in principle, can be made met to a great extent by controlling or tailoring the defect structure of the oxide. This paper reviews the defect structure, nonstoichiometry as a measure of the total defect concentration, and the defect relaxation kinetics of complex oxides that are currently involved in a variety of growing applications today.

Key words: Defect structure, Nonstoichiometry, Nonstoichiometry Relaxation, Complex Oxides, SOFC

1. Introduction

Crystalline oxide materials have long garnered a vast range of technological interest in optical, electrical, magnetic, thermal, chemical, and electrochemical applications. They often comprise no less than three components in at least three sublattices, and tend to be even more complex in terms of the number of components and sublattices. The simplest examples may be those with a perovskite structure (ABO₃) or a spinel structure (AB₂O₄).

For all applications of complex oxides, knowledge and control of their defect structure is essential to endow them with their necessary functions as well as to design and/or optimize the processing route of relevant devices. By the defect structure, we mean the types, concentrations and spatial distributions of mainly point defects. For the best electrochemical performance of an SOFC electrode oxide, for example, the oxide should be defect-chemically processed to have high oxide ionic conductivity as possible while suppressing cationic mobility as much as possible, in addition to a sufficiently high level of electronic conductivity. Another example may be positive temperature coefficient resistors (PTCR) based on BaTiO₃; the interior of BaTiO₃ grains should be made n-type semiconducting by doping donor impurities and the grain boundaries electrically insulating by oxidation. The thickness of a grain boundary insulation layer should be carefully controlled for optimum PTCR performance by appropriately adjusting the magnitude and distribution of oxygen nonstoichiometry during cooling after sintering. A further example may be BaTiO₃-based multilayer ceramic capacitors (MLCC) employing base metal electrodes (e.g., Ni); it should be sintered in a reducing atmosphere to avoid oxidation of the base metal while suppressing the reduction-generated electrons and oxygen vacancies in order to retard the insulation-resistance degradation while the devices are in service. In a sense, control or tailoring of the defect structure is similar to blowing the show into the body, an art of making oxides functionally alive.

The basic principle behind the control or tailoring of the defect structure is that point defects are thermodynamically stable and hence, their concentrations, as thermodynamic equilibrium properties, can be uniquely determined by the independent thermodynamic variables, namely, temperature, pressure and compositions or their conjugate chemical potentials of the system. This is a basic thermodynamic postulate, that may even be called the "-1st" law of thermodynamics. Thus, by adjusting the temporal and spatial distribution of these thermodynamic variables, one can, in principle, adjust the temporal and spatial distribution of defects.

Defects are not a conserved entity: they can be annihilated or generated normally via solid state diffusion from or to repeatable growth sites such as surfaces, grain boundaries and dislocations. Solid-state diffusion is a time and energy-consuming process. One may, thus, kinetically cheat the defect structure by adjusting the time rate of the thermodynamic variables. The latter is often taken advantage of in actual processes to freeze-in a non-equilibrium defect structure for the purpose of controlling the properties.

In this article, we will consider the thermodynamic and kinetic aspects of the defect structure in complex oxides with application in mind. As a prototype of complex oxides, this paper specifically refers to BaTiO₃ among others because, to the best of the author's knowledge, the experimental data related to BaTiO₃ have been extensively and consistently documented. This is not intended as an exhaustive literature review, but propose instead to convey the
thermodynamic and kinetic behavior of the defect structure in complex oxides. Even if BaTiO$_3$ is referred to exclusively here, the information can easily apply to other complex oxide systems with minor modifications.

The configuration of the article will be as follows. In Section 2, we will summarize how to calculate the equilibrium defect structure of the prototype complex oxide as a function of independent thermodynamic variables. Once a batch composition in terms of the component oxides, say BaO and TiO$_2$, is formulated, the only possible control of the defect structure during processing is normally via the exchange of the volatile component, for instance oxygen during heat treatment. This adjusts the oxygen nonstoichiometry that eventually governs the concentration of charge carriers, oxygen vacancies, electrons, and holes that often drastically affect the performance of the oxide-based devices. In Section 3, we will see how oxygen nonstoichiometry, as a measure of the concentration of electronic carriers, varies with the thermodynamic variables and its defect-chemical implications. Adjustment of oxygen nonstoichiometry can be achieved to a great extent by chemical diffusion processes under an oxygen potential gradient imposed during actual processing of an oxide or related devices. Section 4 examines how oxygen nonstoichiometry relaxes in an oxygen potential gradient in connection with the defect structure.

2. Defect Structure

The logical framework to calculate defect structure of a complex oxide has earlier been laid by Wagner and Schmalzried.[2,5] The basic idea behind is to solve the simultaneous equations involving concentrations of the structure elements, be they regular or irregular, that are based on a series of constraints of internal (thermal) equilibria, external (particle exchange) equilibria, crystal structure preservation, charge neutrality, and mass conservation (when doped). The internal equilibria are determined by temperature only under ambient pressure ($P=1 \text{ atm}$), but the external ones are determined by the independent activities of the chemical components in addition to the temperature. We will, thus, end up with a concentration as a function of the intensive thermodynamic variables of the given system, viz., temperature and independent activities of the components. We will apply this idea to calculate the defect structures of BaTiO$_3$, pure, acceptor-doped and donor-doped cases, respectively.

2.1. Pure case

Let us first consider pure BaTiO$_3$. For a ternary system, there are two composition variables, e.g., mole fractions of Ti and O. When there are three sublattices, however, it is more convenient to choose the molecular ratio of the component oxides, BaO and TiO$_2$ and the equivalent ratio of the non-metallic components to the metallic components$^{16}$ or

$$1+\eta=\frac{[\text{Ti}]}{[\text{Ba}]}=\frac{1}{3+\delta} \frac{[\text{O}_2]}{[\text{Ba}]+4[\text{Ti}]}$$

(2.1)

where $[\ ]$, represents the total concentration of the component therein. The lattice molecule may then be represented more appropriately as

$$\text{BaTi}_{1+\eta} \text{O}_{3+\delta}$$

(2.2)

where $\eta$ is called the deviation from the molecularity($\eta=0$) or nonmolecularity, and $\delta$ the deviation from the stoichiometry($\delta=0$) or nonstoichiometry of the compound. Any thermodynamic equilibrium property of the system is given as a function of independent thermodynamic variables of the system under the atmospheric pressure, temperature (T), the activity of a component oxide, say, TiO$_2$(a$_{\text{TiO}_2}$) and the activity of oxygen (a$_{\text{O}_2}$) or equivalently by their conjugate variables $\eta$ and $\delta$, considering the Gibbs-Duhem equation for the system.

One may start by conjecturing the possible defects of the oxide from its structural and energetic considerations. For the system of perovskite structure, the interstitial defects may be ruled out and hence, the structure elements the concentrations of which we want to know may be the irregular structure elements: V$_{\text{Ba}}^+$, V$_{\text{Ti}}^-$, V$_{\text{O}}^-$, O$_{\text{Ba}}^-$, O$_{\text{Ti}}^+$, O$_{\text{O}}^0$; in terms of the Kröger-Vink notation.

Letting [S] denote the concentration (in number/cm$^3$) of the structure element S ([$e^+]$=n, [$h^+$]=p), one may formulate all the constraints assuming an ideal dilute solution behavior of defects as:

(i) Internal equilibria:

$$0=e^+ + h^- ; \quad K_e=n_p$$

(2.3)

$$0=V_{\text{Ba}}^++V_{\text{Ti}}^- + 3V_{\text{O}}^-; \quad K_{\text{V}}=\frac{[V_{\text{Ba}}^+][V_{\text{Ti}}^-][V_{\text{O}}^-]^3}{[V_{\text{Ba}}][V_{\text{Ti}}][V_{\text{O}}]^3}$$

(2.4)

(ii) External equilibria:

$$O_{\text{Ba}}^0 = V_{\text{O}}^- + 2e^- + \frac{1}{2}O_2(g); \quad K_{\text{t}}=[V_{\text{O}}^-]^{n/2}a_{\text{O}}^{1/2}$$

(2.5)

$$\text{TiO}_2 = \text{Ti}_{\text{Ti}}^++2O_{\text{O}}^0 + V_{\text{Ba}}^++V_{\text{O}}^-; \quad K_{\text{t}}=\frac{[V_{\text{Ba}}^+][V_{\text{O}}^-]^3}{[V_{\text{Ba}}][V_{\text{O}}]^3}$$

(2.6)

(iii) Charge neutrality:

$$n+2[V_{\text{Ba}}^+]+4[V_{\text{Ti}}^-]=p+2[V_{\text{O}}^-]$$

(2.7)

(iii) Structure preservation:

$$1=[\text{Ba}_{\text{Ba}}]+[V_{\text{Ba}}^+]$$

(2.8)

$$1=[\text{Ti}_{\text{Ti}}^+]+[V_{\text{Ti}}^-]$$

(2.9)

$$3=[O_{\text{O}}^0]+[V_{\text{O}}^-]$$

(2.10)

with $\beta=N_{\text{Ti}}/V_{\text{Ba}}$, $N_{\text{Ti}}$ and $V_{\text{Ba}}$ being the Avogadro number and the molar volume of the system, respectively.

Here, the mass-action law constants are denoted as $K_i(j=\text{Re}, \text{T, S, i})$ which may be represented as

$$K_i = K_i^0 \exp \left( \frac{\Delta H_i}{kT} \right)$$

(2.11)

where $K_i^0$ is the pre-exponential factor and $\Delta H_i$ the enthalpy change of the associated reaction $i$. 


Table 1. Matrix of Majority Disorder Types in the Systems of BaTiO₃. The Top Left Rectangle Demarcated by Thick Solid Lines is for the Pure Case; this Rectangle Plus the Rightmost Column for the Acceptor-doped Case; the Rectangle Plus the Bottommost Row for the Donor-doped Case. A Pair of Signs Omitted at +,0, at each Element are for η and δ: e.g., (+,0) is for η>0 and (0,0) is for η<0.

<table>
<thead>
<tr>
<th></th>
<th>-</th>
<th>n</th>
<th>2[V₉₆⁺]</th>
<th>4[V₉₆⁺]</th>
<th>[A⁺]</th>
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<tbody>
<tr>
<td>p</td>
<td>n=p</td>
<td>0 ; 0</td>
<td>-1/6 ; 1/6</td>
<td>1/6 ; 0</td>
<td>-1/6 ; -1/3</td>
</tr>
<tr>
<td></td>
<td>p=2[V₁₀⁺]</td>
<td>1/6 ; 1</td>
<td>1/6 ; 1/6</td>
<td>1/6 ; 0</td>
<td>1/6 ; 1/3</td>
</tr>
<tr>
<td></td>
<td>p=4[V₁₀⁺]</td>
<td>0 ; 4/3</td>
<td>0 ; 1/3</td>
<td>0 ; -1/3</td>
<td>0 ; -1/3</td>
</tr>
<tr>
<td></td>
<td>p=[A⁺]</td>
<td>1/6 ; 1</td>
<td>0 ; 1/2</td>
<td>1/6 ; 0</td>
<td>1/6 ; 1/3</td>
</tr>
<tr>
<td></td>
<td>[V₁₀⁺]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td></td>
<td>[V₂₀⁺]</td>
<td>-1/2 ; 0</td>
<td>-1/2 ; 0</td>
<td>-1/2 ; 0</td>
<td>-1/2 ; 0</td>
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<tr>
<td></td>
<td>[A⁻]</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
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<tr>
<td></td>
<td>[A⁻]</td>
<td>-1</td>
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</tbody>
</table>

It is noted that there are exactly 8 equations (Eqs. 2.3-2.10) for 8 unknowns (V₁₀⁻, V₉₆⁻, V₀⁻, e⁻, h⁺, BaBa⁺, Ti₁⁺, O⁻). As the concentrations of irregular structure elements are normally much smaller than those of regular structure elements, Eqs. 2.8 to 2.10 turn trivial (i.e., [BaBa⁺]=[Ti₁⁺]=[O⁻]=0), and hence, one may delete the regular structure elements from the list of the unknowns. Then, note that when one starts with "q" irregular structure elements in a c-component system, there would always be (c-1) external equilibrium conditions and (q-o) internal equilibrium conditions and 1 charge neutrality condition to determine all those n unknowns completely.

In principle, one can solve the equations simultaneously for each defect concentration in terms of K₂(T), a₁₂₀₂ and a₀₂ or

$$[S]=a_{1202}^m a_{0202}^n K^s$$  \hspace{1cm} (2.12)

However, it is usually prohibitively messy; the culprit is that the algebraic structure of the charge neutrality condition, Eq. 2.7, is different from the rest, Eqs. 2.3-2.6. The normal practice is, thus, to approximate the charge neutrality condition by a limiting condition or in terms of an oppositely charged pair of disorder in the majority (Brouwer approximation) depending on the thermodynamic conditions.

All the possible types of majority disorder may be distinguished by constructing a matrix with the positively charged disorders as row and the negatively charged ones as column (vice versa, of course) as shown in Table 1. In the case of pure BaTiO₃, there can be 2 x 3 elements or 6 possible majority disorder types.

By using the limiting charge neutrality condition in terms of a majority disorder pair in Table 1, one can now solve with no algebraic awkwardness at all each defect concentration in the form of

$$[S]=a_{1202}^m a_{0202}^n K^s$$  \hspace{1cm} (2.13)

The numerical values for the exponents "m" and "n" (not to be confused with the electron concentration in Eq. 2.3) in each majority disorder regime are listed (in the form of m : n at each element) in Table 2.

In order to construct a complete picture of defect structure against the thermodynamic variables particularly a₁₂₀₂ and a₀₂ over their entire ranges, one should combine these piecewise solutions, Eq. 2.13 in appropriate order. For this purpose, one should first know the distribution of the majority disorder types in the thermodynamic configuration space of loga₁₂₀₂ vs. loga₀₂ at fixed temperature. A simple method to find the configuration of the majority disorder types goes as follows:

For the present system, Eq. 2.2, the nonmolecularity may

Table 2. Numerical Values for m and n Such that [S]=a₁₂₀₂^m a₀₂^n K^s in Each Majority Disorder Regime of Table 1

<table>
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<tbody>
<tr>
<td>n</td>
<td>0 ; 0</td>
<td>-1/6 ; 1/6</td>
<td>1/6 ; 0</td>
<td>-1/4 ; 1/4</td>
<td>0 ; 1/2</td>
<td>0 ; 1/2</td>
<td>0 ; 0</td>
</tr>
<tr>
<td>p</td>
<td>0 ; 0</td>
<td>1/6 ; 1/6</td>
<td>1/6 ; 0</td>
<td>1/6 ; 1/6</td>
<td>1/6 ; 1/6</td>
<td>0 ; 0</td>
<td>0 ; 0</td>
</tr>
<tr>
<td>[V₁₀⁺]</td>
<td>1/2 ; 1</td>
<td>0 ; 4/3</td>
<td>0 ; 1/3</td>
<td>0 ; 1/3</td>
<td>0 ; 1/3</td>
<td>0 ; 0</td>
<td>0 ; 0</td>
</tr>
<tr>
<td>[V₂₀⁺]</td>
<td>1 ; 0</td>
<td>0 ; 1/3</td>
<td>1/6 ; 1</td>
<td>1/6 ; 1</td>
<td>1/6 ; 1</td>
<td>0 ; 0</td>
<td>0 ; 0</td>
</tr>
<tr>
<td>[V₀⁺]</td>
<td>-1/2 ; 0</td>
<td>1/2 ; 0</td>
<td>0 ; 1/3</td>
<td>0 ; 1/3</td>
<td>0 ; 1/3</td>
<td>0 ; 0</td>
<td>0 ; 0</td>
</tr>
<tr>
<td>[A⁻]</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
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<tr>
<td>[A⁻]</td>
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</tr>
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</table>

Calculating the values of $[S]$ using the above equations, we can find the majority disorder regimes for each temperature and composition. For example, when the temperature is 1000 K, and the composition of BaTiO₃ is 0.1, the majority disorder type is acceptor-doped.
be represented in terms of irregular structure elements, due to Eqs. 2.1 and 2.8-2.10 as

\[ \beta = [V_0] - [V_{\text{Ti}}] \]

(2.14)

as normally $[S]/[P] < 1$ if S is irregular. The nonstoichiometry, on the other hand, may be written as

\[ \beta = [V_0] - [V_{\text{Ti}}] - 2[V_{\text{Ti}}] = \frac{1}{2}(n - p) \]

(2.15)

for the same reason. The second equality is due to the charge neutrality condition, Eq. 2.7.

For each of the majority disorder types in Table 1, one can then determine by using Eqs. 2.14 and 2.15 whether $\eta$ and $\delta$ are respectively larger than 0 (denoted as +), close to 0 (denoted as 0) or smaller than 0 (denoted as -). The results, pairs of $-0$ and + are given in the form of, e.g., (- ; 0) to each element in Table 1 where the first symbol is for $\eta$ and the second for $\delta$. In this identification, one should be aware that for the majority disorder type for which $\eta$ can be both + and - as, e.g., for $n=p$ or $n=2[V_0]$, one may set $\eta=0$.

There can be three regions along the axis of log $a_{\text{O}}$; $\delta > 0$ (oxygen deficit); $=0$ (near stoichiometry); $<0$ (oxygen excess) with increasing $a_{\text{O}}$. Also three regions along the axis of log $a_{\text{TiO}_2}$; $\eta < 0$ ($\text{TiO}_2$ deficit); $=0$ (near molecularity); $>0$ ($\text{TiO}_2$ excess) with increasing $a_{\text{TiO}_2}$. The configuration plane may, thus, be divided into 9 regions. One can then assign each majority disorder type to the region corresponding to its sign combination for ($\eta$; $\delta$) in Table 1. It happens quite often that multiple types fall in one region usually as the number of majority disorder types increase over 9. Again old wisdoms in help one not to get lost in finding the appropriate sequence of the majority disorder types. They are:

Rule 1. Near molecularity and stoichiometry region (0; 0): It is to be occupied by an intrinsic majority disorder type, either electronic or ionic disorder pair depending on which is energetically more favorable. In the present pure case, it depends on whether $K^{1/2}_1 > K^{1/5}_1$ or $K^{1/2}_1 < K^{1/5}_1$. Consequently intrinsic electronic and ionic disorder pairs normally do not fall congruently.

Rule 2. Other regions: The sequence in a given region outside the region (0; 0) is to be determined by the continuity principle, that is, any two neighboring regimes of majority disorder should have one defect of the defect pairs in common.
Rule 3. Majority disorder regime boundaries: Once the majority disorder types are located sequentially in the configuration plane of \( \log a_{O} \) vs. \( \log a_{\text{O}_2} \), the two neighboring regimes of majority disorder meet in line when one defect of the two pairs is in common and otherwise at point. In the 3-dimensional space of \( \log a_{O} - \log a_{\text{O}_2} - 1/T \), the former would be a plane and the latter a line. We may call these the allocation rules. By applying these rules, one can construct the configuration planes as shown in Fig. 2.1 (a) and (b) for the case of \( K^{1/2} - K^{1/2} \) and \( K^{1/2} - K^{1/2} \), respectively. Up to now, however, there has appeared no experimental evidence for BaTiO\(_3\), which may even hint a possibility of \( n=p \) being the majority disorder under any thermodynamic condition.

2.2. Acceptor-doped case

Next we will consider BaTiO\(_3\) doped with fixed amount (x) of acceptor impurities A on, e.g., cation sites (generically denoted as \( A^+_c \)). Specifically, they are assumed to be trivalent substituting Ti or \( A^+_c \), e.g., Al\(_{Ti}\). The lattice molecule may then be written as

\[
\text{BaTi}_{1-x}A_x\text{O}_{3-x/2+2n/3} \tag{2.16}
\]

As one more defect species \( A^+_c \) is added, one needs one more constraint in addition to those for the pure case: that is mass conservation or

\[
[A^+_c] = \beta x \tag{2.17}
\]

The charge neutrality condition Eq. 2.7 and the site conservation conditions Eq. 2.9 should be accordingly modified, respectively, as

\[
n + 2[V_{O}^6] + 4[V_{Ti}^{5+}] + [A^+_c] = p + 2[V_{O}^0] \tag{2.18}
\]

\[
\frac{1}{2}[\text{Ba}^5_{Ba}] + [V_{Ti}^{5+}] + [A^+_c] \tag{2.19}
\]

In addition, while the nonmolecularity is still the same as Eq. 2.14, the nonstoichiometry should be modified due to Eq. 2.1 as

\[
\beta = [V_{O}^0] - [V_{O}^{2+}] - 2[V_{Ti}^{5+}] - \frac{1}{2} [A^+_c] = \frac{1}{2}(n-p) \tag{2.20}
\]

From Eq. 2.18 or from the matrix in Table 1, one can immediately distinguish \( 3 \times 3 \) limiting conditions or 8 possible majority disorder types, but one should note that any intrinsic disorder type, \( n=p \) in the present case, cannot occupy the near molecularity-stoichiometry region \((0;0)\), because obviously \([A^+_c] > K^{1/2} - K^{1/2}\) or it would otherwise not be extrinsic to the doped acceptors. Again following Rules 1-3, one can construct the configuration plane of the majority disorder types as in Fig. 2.1(c) and in each regime, the values for the exponent \( m \) and \( n \) of Eq. 2.13 are given in Table 2.

2.3. Donor-doped case

Let us assume that our BaTiO\(_3\) is now doped with a fixed amount (y) of donor impurities D on, e.g., the cation sites (D\(_c\)). They are again assumed to be fixed-valent, but this time occupying Ba-site instead, or D\(_{Ba}\), e.g., La\(_{Ba}\). Then, the lattice molecule may be represented as

\[
\text{Ba}_{1-y}D_y\text{Ti}_{1-n}O_{3-n/2+2n/3} \tag{2.21}
\]

As one more unknown \([D_{Ba}]\) is added similarly to the acceptor-doped case, one mass-conservation equation for the dopant is added to Eqs. 2.3-2.6 as

\[
[D_{Ba}] = \beta y \tag{2.22}
\]

In addition, the charge neutrality and site conservation conditions, Eqs. 2.7 and 2.8 are modified, respectively, to

\[
n + 2[V_{O}^6] + 4[V_{Ti}^{5+}] = p + 2[V_{O}^0] + [D_{Ba}] \tag{2.23}
\]

\[
\frac{1}{2} = [\text{Ba}^5_{Ba}] + [V_{Ti}^{5+}] + [D_{Ba}] \tag{2.24}
\]

The nonstoichiometry subsequently takes the form

\[
\beta = \frac{1}{2}(n-p) = [V_{O}^0] - [V_{O}^{2+}] - 2[V_{Ti}^{5+}] - \frac{1}{2}[D_{Ba}] \tag{2.25}
\]

while the nonmolecularity still remains the same as Eq. 2.14.

From Eq. 2.23 or Table 1, one can distinguish \( 3 \times 3 \) possible limiting conditions or possible majority disorder types. But, again the intrinsic disorder type \( n=p \) is ruled out from the near molecularity-stoichiometry region \((0;0)\) in the configuration plane and hence, one is left with 8 majority disorder types. The configuration map of the majority disorder types can be constructed following Rules 1-3 as in Fig. 2.1(d). The reader may wish to check from the maps in Fig. 2.1 how those rules are working.

2.4. Two-dimensional representations of defect concentrations

Eq. 2.13 is basically a four dimensional representation (under a fixed total pressure) of defect structure, that is not so easy to visualize with ordinary vision. Normal practice is, thus, to represent in two dimensions: \( \log [S] \) vs. \( \log a_{O_2} \) (at fixed \( a_{O_2} \) and \( T \)), \( \log [S] \) vs. \( \log a_{O_2} \) (at fixed \( a_{TiO_2} \) and \( T \)), or \( \log [S] \) vs. \( 1/T \) (at fixed \( a_{TiO_2} \) and \( a_{O_2} \)).

By combining the piecewise solutions, Eq. 2.13 with \( m \) and \( n \) values as given in Table 2 in accord with the configuration of the majority disorder types in Fig. 2.1, one can easily draw \( \log [S] \) vs. \( \log a_{TiO_2} \) (at fixed \( T \) and \( a_{O_2} \)) or \( \log a_{O_2} \) (at fixed \( a_{TiO_2} \) and \( T \)). The cross section along a horizontal dotted line in each of Fig. 2.2(a)-(d) (designated as “h”), for example, is shown in Fig. 2.2(a)-(d), which are nothing but \( \log [S] \) vs. \( \log a_{TiO_2} \) (at fixed \( T \) and \( a_{O_2} \)). Similarly, \( \log [S] \) vs. \( \log a_{O_2} \) (at given \( T \) and \( a_{TiO_2} \)) are shown in Fig. 2.3(a)-(d) which are the cross sections along the vertical dotted lines denoted as “v” in Fig. 2.1(a)-(d), respectively.

The reader is reminded that the representations, Figs. 2.2 and 2.3, are for the systems in equilibrium internally (Eqs. 2.3 and 2.4) as well as externally (Eqs. 2.5 and 2.6). In many cases, however, the external equilibria are often suspected for kinetic reasons. For BaTiO\(_3\) and the like, for example,
chemical diffusion of oxygen is normally much faster than the metallic components and hence, while oxygen exchange equilibrium, Eq. 2.5, can be readily achieved, the metallic component exchange equilibrium, Eq. 2.6, can often be hardly achieved. If it is the case, $a_{nO_2}$ may not be held fixed while $a_{OP}$ varies. The extreme situation may be the case in which the system is closed with respect to the metallic components exchange so that the nonmolecularity $\eta$, instead of $a_{nO_2}$, remains fixed by the initial batch composition across the entire range of log $a_{OP}$. Depending largely on temperature, this situation may be more realistic than the complete thermodynamic equilibrium. One, thus, often needs to know how defect structure varies against $a_{OP}$ while $\eta$, instead of $a_{nO_2}$, is held constant. Old wisdom has already considered this problem. We will now transform log $[S]$ vs. log $a_{OP}$ at fixed $a_{nO_2}$ in Fig. 2.3 to those at fixed $\eta$ to see how they appear.

To make the situation simpler, let us assume that the initial batch composition, whether doped or not, is with $a_{nO_2}$ deficit ($\eta<0$) such that

$$-\beta \eta = [V^{m}_{O_n}] > [V^{m}_{O_n}]$$  \hspace{1cm} (2.26)

Then, one can immediately dictate the variation of $-\eta$ versus $a_{OP}$ at fixed $a_{nO_2}$ by following the variation of $[V^{m}_{O_n}]$ in Fig. 2.3(a)-(d). It is noted there that even if $a_{nO_2}$ is held fixed, the nonmolecularity is changing with oxygen activity, meaning that material has to be exchanged with the surrounding for keeping the system in the external equilibrium.

In each of the majority disorder regimes, one can obtain from Eq. 2.13 for $[S]=[V^{m}_{O_n}] \approx -\beta \eta$,

$$a_{nO_2} = a_{OP}^{m,n} (-\beta \eta)^{1/2} |K^m|^{1/2}$$  \hspace{1cm} (2.27)

Each defect concentration in Eq. 2.13 can then be transformed, by replacing $a_{nO_2}$ with Eq. 2.27, into a form.

**Fig. 2.2.** Log $[S]$ vs. log $a_{nO_2}$ (a)-(d) corresponding to the horizontal dotted lines designated as "h" (fixed $a_{OP}$) in Fig. 2.1(a)-(d), respectively.
Fig. 2.3. Log [S] vs. log $a_{O_2^+}$ (a)-(d) corresponding to the vertical dotted lines designated as $\nu$ (fixed $a_{O_2^+}$) in Fig. 2.1(a)-(d), respectively.

$$[S] = a_{O_2^+}(-\beta n)^{3/3} K_1^{1/2} K_2^{1/2}$$ for $S = V_{T_1}^{1/2}$

By combining these piecewise solutions in accord with the appropriate sequence of the majority disorder types, in principle, one can transform Fig. 2.3 to those for fixed $\eta$. The sequence of the majority disorder types for fixed $\eta$ will remain the same as that for fixed $a_{O_2^+}$ due to Le Châtelier’s principle.

$$\left( \frac{\partial (-\beta n)}{\partial \ln a_{TiO_2^+}} \right)_{\ln a_{O_2^+}} > 0$$

Now let us suppose that the fixed nonmolecularity is such that

$$K_1^{1/2}, K_2^{1/2} << -\beta n << [A_{O_1}], [D_{Ba}]$$

Then, for the pure undoped case in Fig. 2.3(a), the regime of $n = p$ cannot be seen and the sequence of majority disorder types subsequently turn the same as that in Fig. 2.3(b) whether $K_1^{1/2} >> K_2^{1/2}$ or $K_1^{1/2} << K_2^{1/2}$. The latter is transformed as in Fig. 2.4(a), where it is noted that $[V_{Ti}^{1/2}]=-\beta n$ is flat against log $a_{O_2^+}$. For the acceptor-doped case Fig. 2.3(c), the majority disorder regime of $p = 4[V_{Ti}^{1/2}]$ is impossible because $[V_{Ti}^{1/2}]=-\beta n$ is fixed. Consequently, the transformed plot should be as in Fig. 2.4(b). For the donor-doped case of Fig. 2.3(d), the majority disorder regime $[D_{Ba}] = 4[V_{Ti}^{1/2}]$ cannot exist due to the assumption on $\eta$, Eq. 2.30 and the regime $p = 4[V_{Ti}^{1/2}]$ either for the same reason as in the acceptor-doped case. Fig. 2.3(d) is, thus, transformed as in Fig. 2.4(c).

Actually, any shift of disorder regime with the component activities is only made possible by exchanging the chemical components, say O and Ti (or Ba) with the surrounding. Otherwise, the shift itself would be impossible. For example, when our donor-doped BaTiO$_3$ undergoes a shift from $[D_{Ba}] = 4[V_{Ti}^{1/2}]$ to $n = [D_{Ba}]$ at a fixed $a_{TiO_2^+}$ (see Fig. 2.3(d)), the lattice molecule changes nominally from Ba$_{y_{Ti}}$D$_{Ta-y_{Ta}}$O$_z$ to Ba$_{y_{Ti}}$D$_{Ta}$TiO$_z$, that is, $\eta$ changes from $-y_{/2}$ to 0, indicating that Ti is supplied from (or Ba is drained to) the surrounding. This is why we have limitations on the availability of the majority disorder regimes for the partially closed cases ($\eta =$constant) in Figs. 2.4(b) and (c). One may take advantage of this fact to tell whether the system is closed with respect to metallic component exchange: If a donor-doped BaTiO$_3$ exhibits an $a_{O_2^+}$-region where $n = a_{O_2^+}$ in agreement
with Fig. 2.3(d), for example, then one may say that the system remains open to keep $\alpha_{\text{p}O_2}$ rather than $\eta$, constant, indicating the presence of a second phase.\(^{16}\)

Finally, one may be interested in the variation of $\alpha_{\text{p}O_2}$ with $\alpha_{\text{p}}$ while $\eta$ is held fixed. It is calculated via Eq. 2.27 or Eq. 2.6 or more easily in the present case as

\[
a_{\text{p}O_2} = K_T \left[ -\beta \eta^{-1} V_0 \right]^{2}
\]

due to the external equilibrium

\[
\text{TiO}_2 + 2\text{O}_2 = \text{V}_{\text{p}O}^n + 2\text{V}_0 + \text{TiO}_2
\]

that is another aspect of (thus redundant with) Eq. 2.6 or $K_e K_v = K_o$. One can now draw in Figs. 2.4 (a)-(c) the variations of log $\alpha_{\text{p}O_2}$ simply by following that of $[V_0]$, but with twice its slope in the opposite sense.

### 2.5 A further complication: hole trapping

Up to now, we have considered that all donors or acceptors, whether intrinsic or extrinsic, are fully ionized. As temperature is lowered, however, those centers particularly of extrinsic origin tend to trap electrons or holes. Once electronic carriers are fully trapped, the defect-sensitive properties are often altered appreciably at low temperatures in particular.\(^{16}\) The trapping effect may be ingeniously taken advantage of in designing the composition of actual material for special functions. Here we will consider, for example, hole trapping by fixed-valent acceptor impurities, say, $\text{A}^0_{\text{p}}$.

When hole trapping is no longer negligible and hence, the concentration of the trapped holes, say $[\text{A}^0_{\text{p}}]$ is of concern, one add to Eqs. 2.3-2.6 one more equilibrium condition, that is the internal equilibrium condition with respect to hole trapping or ionization equilibrium condition of the acceptors,

\[
\text{A}^0_{\text{p}} + \text{h}^+ = \text{A}^+_{\text{p}}
\]

[Mass conservation constraint, Eq. 2.17 is accordingly modified as

\[
[A] + [\text{A}^0_{\text{p}}] = [\text{A}]
\]

The charge neutrality equation, however, remains the same or Eq. 2.18 because the trapped holes make the acceptor centers only neutral ($\text{A}^0_{\text{p}}$) in the present case. Otherwise, it would have to be modified to include the acceptors with different effective charges due to hole trapping.

One may define the trapping factor $\chi^{-1}$ as

\[
\chi^{-1} = \frac{[\text{A}^0_{\text{p}}]}{[\text{A}]}
\]

Two extreme cases are distinguished. When $\chi^{-1} << 1$, the concentration hierarchy will be such that

\[
[A^+_{\text{p}}] >> [\text{A}] > [\text{A}^0_{\text{p}}]
\]

and the defect structure is essentially the same as in Fig. 2.3(c) or Fig. 2.4(b) only with $[\text{A}^0_{\text{p}}]$ added as a minority disorder if one likes. When $\chi^{-1} >> 1$, on the other hand, most of holes are trapped and the concentration hierarchy in the near stoichiometry regime ($2[V_0] = [\text{A}^0_{\text{p}}]$) turns to

\[
[A^+_{\text{p}}] >> [\text{A}] > [\text{A}^0_{\text{p}}] >> p
\]

As $\alpha_{\text{p}}$ increases further, the trapped centers come to overwhelm the acceptor impurities or
Fig. 2.5. Defect structure for the acceptor-doped case (corresponding to Fig. 2.3(c) or Fig. 2.4(b)) with holes trapped fully \( \chi^{1/3} \).

\[
[A^+_D] = [A^*_D] > [A^-] > [A^+] > [A^+_D] \quad (2.38)
\]

As \( a_{\text{O}_2} \) increases even further, the charged disorders in majority will finally become \( p = [A^-] \). The defect structure is as shown in Fig. 2.5, in which the portion corresponding to the concentration hierarchy of Eq. 2.37 is essentially the same as given by Waser \( \text{for SrTiO}_3 \).

2.6. Defect structure and reality

Experimental studies on defect structure of complex oxides are very much limited compared to those on binary systems. It is, thus, fair to say that our understanding of the defect structure of the complex oxides is still far from complete. For example, BaTiO_3 is one of the most studied systems, but we still do not know whether donor impurities, say, La\text{Ba} are compensated by \( V^+_{\text{T}_1} \) or \( V^+_\text{O}_2 \) or both in the ion-compensation regime. Furthermore, it has been believed from a structural point of view that Ba is more mobile than Ti, but a most recent study \( \text{shows that Sr substituting Ba and Zr substituting Ti are all comparatively mobile at elevated temperatures, leaving the defect structure more puzzling.} \)

Information on the defect structure has been obtained usually from the observations of defect-structure-sensitive properties against the component activities, say, \( \text{a}_{\text{Ba}} \) and \( \text{a}_{\text{O}_2} \), in particular. The simplest and straightforward properties may be electrical conductivity and (self- or impurity-) tracer diffusivities among others because they are directly proportional to the concentrations of relevant defects in the majority. For the system of BaTiO_3, for example, a multitude of studies have been made on the electrical conductivity against \( \text{a}_{\text{O}_2} \)(see, e.g. Ref. 8), but never done against \( \text{a}_{\text{Ba}} \). The latter may be experimentally extremely difficult to control if not impossible. Cation tracer diffusion study against oxygen activity has just been started. \( \text{Even for the conductivity studies, it is not always clear whether \( \text{a}_{\text{Ba}} \) or \( \eta \) is held fixed during the measurement. The system under examination is, thus, likely ill-defined thermodynamically in the strictest sense.} \)

For the system of BaTiO_3, the equilibrium conductivity has been the most extensively documented (see, e.g., Refs. 8, 10 and 11) over the experimentally viable range of \(-20 < \log a_{\text{O}_2} \leq 0\) at elevated temperatures, but the remaining variable, \( a_{\text{O}_2} \) or \( \eta \) has not been explicitly specified. Fig. 2.6 shows the typical results for the pure \( \text{(a)} \), acceptor \( (A^-) \)-doped \( \text{(b)} \) and donor \( \text{(LaBa)} \)-doped case \( \text{(c)} \), respectively.

The conductivity is mostly attributed to electronic carriers, thus proportional to \( n \) or \( p \) depending on which is in the majority against \( a_{\text{O}_2} \) and hence, \( \alpha_{\text{O}_2} \) \( \leq a_{\text{O}_2} \) due to Eq. 2.12 or Eq. 2.28 in each disorder regime. It has always been found for the undoped and acceptor-doped cases all alike that over the entire range of oxygen activity examined, the oxygen exponent "\( m \)" takes a value close to \(-1/6, -1/4\) and \(+1/4\) in sequence with increasing \( a_{\text{O}_2} \). For the acceptor-doped case, this sequential variation is no doubt in agreement with the sequential shift of the majority disorder types from \( n=2[V^+_\text{O}_2] \) to \( 2[V^+_\text{O}_2]=[A^-] \) with increasing \( a_{\text{O}_2} \) as shown in Fig. 2.3(c) or Fig. 2.4(b). For the undoped case, however, the interpretation of the same \( n \)-sequence is not so straightforward because depending on \( a_{\text{O}_2} \) or \( \eta \), there can be next to the \( n=2[V^+_\text{O}_2] \) regime where \( \eta \approx \text{a}_{\text{O}_2} \), two possible ionic disorder regimes, \( [V^+_\text{O}_2]=[V^+_{\text{O}_2}] \) or \( [V^+_\text{O}_2]=[V^+_{\text{T}_1}] \) where \( \eta \approx \text{a}_{\text{O}_2} \) and \( p \approx \text{a}_{\text{O}_2} \), see Fig. 2.1(b) and Table 2 or Fig. 2.3(b). It is not clear yet for the system of "pure" BaTiO_3, the experimental finding of \( \eta \approx \text{a}_{\text{O}_2} \) is due to \([V^+_\text{O}_2]=[V^+_{\text{O}_2}] \) or \([V^+_{\text{T}_1}] \) or even due to the background impurity acceptors. \( \text{This issue may be elucidated by observing the conductivity variations on pure specimens with different nonmolecularity \( \eta \), but the experiment may not be so easy because of the extremely limited range of \( \eta \) of the single phase BaTiO_3.} \)

Furthermore, none of the exclusively p-type regimes, \( (h, A^-), (h, V^+_{\text{T}_1}) \) and \( (h, V^+_{\text{O}_2}) \) has ever revealed itself up to \( a_{\text{Ba}} = 1 \) for the system of BaTiO_3.

For the donor-doped case, on the other hand, the oxygen exponent of the conductivity takes values \( m= -1/6, 0, -1/4 \) in sequence as \( a_{\text{O}_2} \) increases up to 1, see Fig. 2.6(c). This sequence reflects the shift of the majority disorder types from \( n=2[V^+_\text{O}_2] \) (\( m=-1/6 \)) to \( n=[\text{LaBa}] \) (\( m=0 \)) and finally to either \([\text{LaBa}]=2[V^+_{\text{O}_2}] \) or \([\text{LaBa}]=4[V^+_{\text{T}_1}] \) (\( m=-1/4 \)), see Fig. 2.1(d) and Table 2 for the m-values. There seems to be no doubt about the majority disorder types for the former two regimes (\( m=-1/6 \) and 0), but the last, ionic compensation regime is not clear concerning whether \([\text{LaBa}]=2[V^+_{\text{O}_2}] \) or \([\text{LaBa}]=4[V^+_{\text{T}_1}] \). There was once an attempt to elucidate this issue: Yoo et al. \( \text{measured the equilibrium conductivity on the three donor-doped specimens with nominal compositions Ba}_1\text{La}_1\text{Ti}_5\text{O}_{14} \text{(designated as Vp), Ba}_1\text{La}_2\text{Ti}_5\text{O}_{14} \text{(as V2p)} \) and \( \text{Ba}_3\text{La}_2\text{Ti}_5\text{O}_{14} \text{(as E)} \). The results are as shown in Fig. 2.6(c). It has been found that there is a minority second phase for all the three and the p-type conductivity increases up to 16% of the total electronic conductivity at \( a_{\text{O}_2} \approx 1 \). Consequently, no conclusion could be drawn
to the identity of the ionic disorder compensating the doped donor impurities, but it has been concluded that $a_{\text{TiO}_{2}}^\text{p}$ rather than $\eta$, is held fixed as in Fig. 2.3(d) because the region where $n \propto a_{\text{TiO}^2}^{1/4}$ and $p \propto a_{\text{TiO}^2}^{1/4}$ is observed at high oxygen activity region that would otherwise not be seen, see Fig. 2.4(c).

For the quantitative, defect-chemical analyses of all these conductivities in Fig. 2.6, the reader is referred to Refs. 10,11,13,16. It is mentioned in passing that for the case of Al-doped BaTiO$_3$, Fig. 2.6(b), practically all holes are trapped by Al-acceptors at the measurement temperatures.\(^7\) The responsible defect structure is, thus, as given in Fig. 2.5 and the $p$-type conductivity ($m = 1/4$) in Fig. 2.6(b) is essentially due to the trapped holes.\(^7\)

### 3. Oxygen Nonstoichiometry

Eqs. 2.15, 2.20 and 2.25 indicate that whether the system is undoped or doped, its oxygen nonstoichiometry is a measure of the concentrations of electronic charge carriers, $n$ and $p$.

$$\beta \delta = \frac{1}{2} (n - p)$$

(3.1)

Fig. 3.1 shows how the nonstoichiometry alters the trend of defect-sensitive properties such as the electronic electrical conductivity, thermoelectric power and oxygen chemical diffusivity.\(^8\) Thus, the control of oxygen nonstoichiometry during processing is very often crucial to ensure the required properties of an oxide or functions of the device.
Fig. 3.1. Electrical conductivity (a), thermoelectric power (b) and chemical diffusivity (c) of undoped BaTiO$_3$ vs. oxygen nonstoichiometry $\delta$. Note that the stoichiometric composition is the demarcation point between $n$-type and $p$-type behavior. From Ref. 10.

As is expected from Fig. 3.1, either in far oxygen-deficit ($\delta>>0$) or oxygen excess region ($\delta<<0$), the nonstoichiometry variation is rather trivial because $n>p$ or $n<p$. In the near stoichiometry region $\delta=0$, on the other hand, the nonstoichiometry variation is not so trivial because there are both electrons and holes. If electronic carriers are trapped by, e.g., doped impurities, then nonstoichiometry variation is even further informative. We will consider here the most general case, namely, the nonstoichiometry in the near stoichiometry region of the acceptor-doped BaTiO$_3$ with holes trapped.

3.1. Nonstoichiometry in general

For the acceptor-doped BaTiO$_3$ with the lattice molecular formula of Eq. 2.16, the nonstoichiometry has been given as Eq. 2.20 or

$$\beta \delta = [V_0] - [V_{Ba}^+] - 2[V_{Ti}^+] - \frac{1}{2}[A_n]^1,$$  

(3.2)

When the concentration of trapped holes is no longer negligible compared to that of free holes, one may rewrite Eq. 3.2, due to the mass conservation constraint, Eq. 2.34 and the charge neutrality constraint, Eq. 2.18, as

$$\beta \delta = \frac{1}{2} [n - p - [A_n]] = \frac{1}{2}[n - p(1 + \chi^{-1})]$$

(3.3)

where $\chi^{-1}$ is the trapping factor defined as the concentration ratio of trapped holes to free holes in Eq. 2.35. It is noted that the stoichiometric composition $\delta=0$ falls, in general, at
n = p(1 + x⁻¹), not at n = p. Only when x⁻¹ → 0, the latter would be the case.

The solutions for the defects in Eq. 3.3 are given in the majority disorder regime of 2[V₀₋→=$\Delta T_I$] (see Table 2) as

\[ p = \chi[A^+_c]\]  \hspace{1cm} (3.4)
\[ n = K_\chi [A^+_c]^{-1} \]  \hspace{1cm} (3.5)
\[ [A^+_c] \approx 2^{1/2} [A^+_c]^{1/2} K_{10}^{1/2} \frac{1}{a_o^2} \]  \hspace{1cm} (3.6)

Eq. 3.3 then takes the form \( ^{17} \),

\[ \beta \delta = -\sqrt{K_\delta^* \sinh \left( \frac{1}{4} \ln \frac{a_o}{a_o^2} \right)} \]  \hspace{1cm} (3.7)

where

\[ K_\delta = K_\delta (1 - x^{-1}) \]  \hspace{1cm} (3.8)
\[ a_o^2 = 4 (1 - x^{-1})^{1/2} K_{10}^{1/2} \]  \hspace{1cm} (3.9)

The latter \( a_o^2 \) is the oxygen activity corresponding to \( \delta = 0 \) or \( n = p(1 + x^{-1}) \), see Fig. 2.5. At this specific oxygen activity \( a_o^2 \), the variation \( \beta \delta \) as a function of \( \ln a_o^2 \) exhibits an inflection or

\[ \left( \frac{\partial^2 (\ln a_o^2)}{\partial \gamma} \right) = 0 \]  \hspace{1cm} (3.10)

This fact actually provides a means to locate the stoichiometric point on a nonstoichiometry isotherm that is measured.\(^{10}\)

Eq. 3.8, in association with Eq. 2.3, indicates that \( K_\delta = n \rho p [A^+_c] \), thus, the latter may be called the "pseudo equilibrium constant for intrinsic electronic excitations." It is noted that only when \( x^{-1} \rightarrow 0, K_\delta \rightarrow K \) and Eq. 3.7 takes the conventional, familiar form:

\[ \beta \delta = -\sqrt{K_\delta^* \sinh \left( \frac{1}{4} \ln \frac{a_o^2}{a_o^2} \right)} \]  \hspace{1cm} (3.11)

This may be the case if the system is pure enough and/or temperature is high enough, see Eq. 2.35. It has often been attempted to determine \( K \) from the nonstoichiometry isotherms via Eq. (3.11) even for a system which bears possible trapping centers, e.g. acceptor impurities whether they are intentionally doped or not. In any case, one should be aware what he actually determines is not the true \( K_\delta \), but \( K_\delta \) in general that is dependent on the type and concentration of the trap centers. One way to estimate \( K_\delta \) is to determine \( K_\delta \) as a function of \( [A] \) via Eq. 3.7 at fixed temperature or \( K_\delta = K_\delta (1 + [A]/K_\delta) \), due to Eqs. 3.8, 2.35 and 2.36. Then, one may take its limiting value as \( [A] \rightarrow -0 \) for the true \( K_\delta \). This, however, has never been experimentally implemented yet.

Once the nonstoichiometry is measured as a function of oxygen activity at different temperatures, the partial molar enthalpy of component oxygen relative to gas oxygen at the standard state, \( \Delta H_O = \frac{\Delta H_0 - \Delta H_{0O}}{2} \) is of some interest. By noting that the relative partial molar Gibbs free energy of component oxygen \( \Delta G_O = \mu_O - \mu_{O_2}^C - \Delta R T \ln a_o^{1/2} \) in Eq. 3.7,

\[ \frac{1}{2} O_2(g) + V_0 = O_2^* + 2h \]  \hspace{1cm} (3.14)
\[ \frac{1}{2} O_2(g) + V_0 + 2e^* = O_2^* \]  \hspace{1cm} (3.15)

They are indistinguishable thermodynamically, but distinguishable defect-chemically. Letting \( K_p \) and \( K_c \) denote the equilibrium constant for these reactions, respectively, they are

\[ K_p = \frac{[V_0]^{1/2}}{[V_0]^{1/2}} \]  \hspace{1cm} (3.16)
Obviously, \( K_n = K_p^2 = K_p K_n^2 \), see Eqs. 2.3 and 2.5, and hence, the associated enthalpy changes \( \Delta H_p \) and \( \Delta H_n \) are interrelated as

\[
\Delta H_n = - \Delta H_p = \Delta H_0 - 2 \Delta H_i \tag{3.17}
\]

Given that the oxidation proceeds in this way, \( \Delta H_0 \) may be taken as a fractional sum of \( \Delta H_p \) and \( \Delta H_n \) such that

\[
\Delta H_0 = \frac{n}{n+p} \Delta H_n + \frac{p}{n+p} \Delta H_p \tag{3.18}
\]

that takes the form, after some algebra using Eqs. 2.3 and 3.1,

\[
\Delta H_0 = \frac{1}{2} (\Delta H_p + \Delta H_n) \frac{\beta \delta}{\sqrt{(\beta \delta)^2 + K_n}} \frac{1}{2} (\Delta H_p - \Delta H_n) \tag{3.19}
\]

This is essentially the same, due to Eq. 3.17, as Eq. 3.12 with \( \chi^{-1} \rightarrow 0 \). One can then immediately identify \( \Delta H_0 (\delta=0) \) to be

\[
\Delta H_0 (\delta=0) = \frac{1}{2} (\Delta H_p + \Delta H_n) \tag{3.20}
\]

If holes are fully trapped or \( \chi^{-1} \rightarrow \infty \), on the other hand, the oxygen incorporation may proceed via Eq. 3.17 and via, instead of Eq. 3.16,

\[
\frac{1}{2} \text{O}_2(g) + V_0^+ + 2A_{\gamma}^+ = \text{O}_2^0 + 2A_{\gamma}^+ \tag{3.21}
\]

with the associated enthalpy \( \Delta H_p = 2 \Delta H_n \), see Eqs. 3.14 and 2.33. In the same line as in Eq. 3.18, one can immediately obtain Eq. 3.12. The same reasoning will also be applied to the case in which electrons are trapped instead of holes.

Eq. 3.18 indicates that when an oxygen atom is incorporated into the lattice, it picks up holes (Eq. 3.14) and electrons (Eq. 3.15) at random depending on their availability. It is, thus, quite natural that the partial molar enthalpy of the component oxygen, \( \Delta H_0 \) is dependent on the relative amount of electrons and holes or the oxygen nonstoichiometry.

The relative partial molar entropy of component oxygen, \( \Delta S_0 \) can also be obtained as a function of \( \delta \) either by using the thermodynamic identity \( [\Delta G_0/\partial T]_0 = -\Delta S_0 \) or by the same argument as in Eq. 3.18,

\[
\Delta S_0 = \frac{n}{n+p} \Delta S_n + \frac{p}{n+p} \Delta S_p \tag{3.22}
\]

but it is not pursued any further. The reader who is interested in is referred to Ref. 19.

### 3.2. Experimental reality

Nonstoichiometry is normally measured by thermogravimetry or coulometric titrometry. In the former, one changes stepwise the oxygen activity in the surrounding of a specimen oxide and monitor the corresponding weight change. In the latter, one incorporates a predetermined amount of oxygen in the form of ionic current and measure the change in equilibrium oxygen activity in the surrounding. For the experimental details, the reader is referred to, e.g., Refs. 19 and 20. In any case, an extreme care should be exercised in order to secure high enough precision to measure the nonstoichiometry variation particularly in the near-stoichiometry region because the nonstoichiometry variation vs. oxygen activity there is the smallest, see Eq. 3.7 or 3.11. The experimental data are usually scarce in this near stoichiometry region, that is probably for this reason. The stoichiometric point, \( a_{0}^* \) in Eqs. 3.7 and 3.11, that is normally determined as in Eq. 3.9, is, thus, not so precisely known for most of oxides whether simple or complex. Here we will show the experimental results on the nonstoichiometry of undoped BaTiO_3.

For the system of undoped BaTiO_3, there were five different data sets against oxygen activity, that are all limited to the range of log \( a_{0} \approx -7 \) over the temperature range of 1000°C to 1340°C. Furthermore, only relative changes in nonstoichiometry, not the absolute values, were given.\(^{21,240}\) Even when the absolute values were reported,\(^{22,23,25,26}\) the stoichiometric points could not be located due to the poor precision. It is only recent\(^{19}\) that the nonstoichiometry has been measured with highest ever precision in the near stoichiometry region including the stoichiometric point \( a_{0}^* \). These results are shown in Fig. 3.3.

The solid curves in the figure are the best fitted to Eq. 3.7 with \( K_i \) and \( a_{0}^* \) as fitting parameters. As is seen, Eq. 3.7 satisfactorily describes the nonstoichiometry, even though the best-fitted values for the fitting parameters are subjected to rather large uncertainties. The latter is again attributed to the still poor precision of the measurement.
Fig. 3.4. Equilibrium oxygen activity vs. reciprocal temperature at different nonstoichiometry values, see Eq. 3.23 in the text. From Ref. 19.

particularly in the vicinity of the stoichiometric point.

The relative partial molar enthalpy of oxygen is evaluated at different nonstoichiometry values by using the thermodynamic identity

$$\frac{\Delta G_0}{RT} = \frac{1}{2} \ln a_{O_2} = \frac{\Delta H_0}{RT} - \frac{\Delta S_0}{R}$$ (3.23)

In Fig. 3.4 is plotted log $a_{O_2}$ vs. reciprocal temperature at different nonstoichiometries. As is seen, it is generally linear for a fixed $\delta$ over the temperature range examined. The relative partial molar enthalpy and entropy of oxygen may then be evaluated from the slope and intercept, respectively. The results of $\Delta H_0$ are as shown in Fig. 3.5. In agreement with Eq. 3.12, the partial molar enthalpy variation is the best fitted as

$$\Delta H_0 (\delta) / \text{kJ mol}^{-1} = -(76 \pm 5) \frac{(272 \pm 38)\delta}{\sqrt{\delta^2 + (3.02 \pm 0.03) \times 10^{-11}}}$$ (3.24)

4. Nonstoichiometry Re-equilibration

When the oxygen activity is changed in the surrounding of a binary oxide $AO_{1-x}$ that has previously been equilibrated with the surrounding, the nonstoichiometry of the oxide changes towards a new equilibrium value. The overall kinetics of this nonstoichiometry re-equilibration process typically consists of the surface reaction step and solid-state-diffusion step in series. The former, gas-solid reaction at the surface is usually regarded as a simple chemical reaction of the first order. The latter diffusion refers to the chemical diffusion of the oxide. We know that there should be one and only chemical diffusion coefficient because there is only one composition variable for the binary oxide (but this is only true when the internal defect equilibrium prevails). For an infinite bar of $AO_{1-x}$ with the square cross section of $2a \times 2a$, for example, the overall re-equilibration kinetics is normally described in terms of the two kinetic parameters, the surface reaction rate constant $k$ and chemical diffusivity $D$ as

$$\frac{\delta(t) - \delta(0)}{\delta(x) - \delta(0)} = 1 - \frac{2L^2 \exp \left[ \frac{k \alpha^2 L^2}{D} \right]}{\sum_{n=1}^{\infty} \frac{n^2 \alpha^2 (n^2 + L^2 + L)}{D}}$$ (4.1)

with $\beta$ such that

$$\beta \tan \beta = L \quad ; \quad L = \frac{\alpha k}{D}$$ (4.2)

Here, $\delta(t)$, $\delta(0)$ and $\delta(\infty)$ are the mean (at time $t$), initial (at $t=0$) and final (at $t=\infty$) value of oxygen nonstoichiometry, respectively. By monitoring the temporal variation of the nonstoichiometry $\delta(t)$ by thermogravimetry or a $\delta$-sensitive property, e.g., electrical conductivity, thus, one can determine the two kinetic parameters. As far as binary systems are concerned, we believe that we understand the relaxation kinetics well. The chemical diffusion, in particular, has long been understood in the light of chemical diffusion theory or in the light of the ambipolar diffusion theory. Concerning the complex oxides, however, it is fair to say that the nonstoichiometry relaxation kinetics and chemical diffusion is not so well understood yet. It is only recently that the kinetics has been examined in a systematic way. We will here present the present understanding of the
Fig. 4.1. Typical nonstoichiometry relaxation of undoped BaTiO$_3$ in its n-type branch of oxygen activity (a) and p-type branch of oxygen activity (b) during reduction and oxidation at 1000°C. The solid lines are the best-fitted to Eq. 4.1 in the text. From Ref. 12.

kinetics, particularly chemical diffusion process first for the undoped or acceptor doped case and then for the donor doped case, in the order of complexity of the relaxation kinetics.

4.1. Undoped or Acceptor-doped BaTiO$_3$
4.1.1. Relaxation behavior and chemical diffusion

It is already pointed out that the undoped and acceptor doped BaTiO$_3$ have the essentially the same defect structure, Fig. 2.3(c) or 2.4(b), in the oxygen partial pressure range that is experimentally viable in practice, -18<log $a_{O_2}$<0. Consequently, the equilibrium conductivities also have the same trend with oxygen activity as shown in Fig. 2.6(a) and (b). Likewise, the relaxation kinetics has also turned out to be essentially the same.

When oxygen partial pressure in the surrounding of the system oxide is abruptly changed either in its n-type branch of oxygen activity ($\sigma_n \propto n_n^{-1/4}$) or in the p-type branch ($\sigma_p \propto p_p^{-1/4}$) in Fig. 2.6(a) or (b), its electrical conductivity, as a direct measure of the oxygen nonstoichiometry ($\delta = n^{1/2} - p^{1/2}$, respectively), relaxes typically as shown in Fig. 4.1 (a) and (b).

These nonstoichiometry relaxations are satisfactorily described by Eq. 4.1, as depicted by the solid curves in Fig. 4.1. The two kinetic parameters are subsequently evaluated as shown in Fig. 4.2.

Upon comparison with the corresponding conductivity in Fig. 2.6(a) or (b), one can see that in the n-p mixed regime of oxygen activity, i.e., in the near vicinity of the conductivity minimum in Fig. 2.6(a) or (b), the overall kinetics is governed mostly by the surface reaction step and otherwise, controlled by the diffusion step. If one totally ignored the surface reaction step or simply took L>>1 in Eq. 4.1 as was often practiced, he would get, despite somewhat larger uncertainty, a diffusion coefficient which appear as shown in Fig. 4.3.

Finally, the true chemical diffusivities that are responsible for the diffusion step in the nonstoichiometry relaxation kinetics have turned out to be as shown in Figs. 4.4(a) and (b) for the undoped BaTiO$_3$ that is polycrystalline, and for the acceptor (A)-doped BaTiO$_3$ that is single crystalline, respectively. It is noted that the diffusivity takes a value up to the order of 10$^{-3}$ cm$^2$/s depending on oxygen activity irrespective of temperature in its range examined and exhibits a maximum in the middle of the oxygen activity range examined. One may be concerned that the diffusivity for the polycrystal BaTiO$_3$ (Fig. 4.4(a)) may have been sub-
\[ \sigma = \sigma_0 + \sigma_m = \sigma_0 \cosh \left( \frac{E_a}{2kT} \right) \]

where \( \sigma_m \) denotes the maximum electronic conductivity, \( \sigma_0 \) is given as

\[ \sigma_0 = \frac{e^2 \tau}{m_e} \]

The solid lines are the best fitted to the experimental data. The fitting parameters, the electronic part of the conductivity, \( \sigma_0 \), are evaluated from the data of the undoped and oxygen-doped BaTiO₃ samples, respectively. The oxygen activity \( \phi \) is calculated as shown in Eq. 1.2.

The electrical conductivity \( \sigma \) is given as in Eq. 3.3.5 or Eq. 2.4.1. The activation energy \( E_a \) is in general given as

\[ E_a = E_a^{(0)} \]

The defect-chemical interpretation of the activation energy is in general given as

\[ E_a = E_a^{(0)} + E_a^{(d)} \]

where \( E_a^{(0)} \) is the activation energy due to the thermodynamic factor.

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Eq. 4.5. Electronic transference number for 1.8 m/o Al-doped BaTiO\textsubscript{3} as calculated from the total conductivity in Fig. 2.6(b). The solid lines are calculated from Eq. 4.4 in the text. From Ref. 13.

thermodynamic factor as

\[ \frac{\delta[V_0]}{\delta \ln aO_2} = \frac{8}{n + p(1 + \chi^2)} \sqrt{\frac{\gamma}{K'_0}} \cosh \left( \frac{1}{4} \ln \frac{aO_2}{aO_2^0} \right) \]  \hspace{1cm} (4.5)

This is nothing but the inverse of the slope of the nonstoichiometry isotherm as in Fig. 3.3. If the system is pure enough, then one may set $\chi^2 = 0$. It has been actually found that $\chi^2 << 1$ for the undoped, and $\chi^2 >> 1$ for the Al-doped case.

Finally by substituting Eq. 4.5 into Eq. 4.3, one obtains

\[ D_0 = \frac{D_0^{0,0}}{\cosh \left( \frac{1}{4} \ln \frac{aO_2}{aO_2^0} \right)} \]  \hspace{1cm} (4.6)

with the factor that is independent of the oxygen activity

\[ \frac{D_0}{D_0^{0,0}} = \frac{RT \sigma_{in}}{2F^2/K_0} \]  \hspace{1cm} (4.7)

The solid lines in Fig. 4.4 are the best-fitted to Eq. 4.6 by using the experimental values for $\sigma_{in}$ and $\gamma$. As is seen, Eq. (4.6) precisely explains the variation of the chemical diffusivity.

4.2. Donor-doped BaTiO\textsubscript{3}

4.2.1. Relaxation behavior and chemical diffusion

The nonstoichiometry relaxation of the undoped or acceptor-doped BaTiO\textsubscript{3} is simple, governed by the chemical diffusion of oxygen and the gas/solid oxygen exchange reaction. It is not different from ordinary binary oxides. This is no longer the case for the donor-doped case. Actually, a long-standing, notorious problem with BaTiO\textsubscript{3} (as well as with any other perovskite oxide) is that kinetics of oxygen nonstoichiometry re-equilibration is usually very much, and sometimes even prohibitively, sluggish for donor-doped BaTiO\textsubscript{3} compared to undoped or acceptor-doped counterparts, and hence, one often hardly knows even whether a donor-doped specimen has been completely equilibrated upon re-equilibration. According to a report, it took more than 4 months to equilibrate a donor(Nb)-doped BaTiO\textsubscript{3} specimen measuring 4 mm x 4 mm x 12 mm with an average grain size of a few microns upon a change of temperature from 1308 to 1216 K in an atmosphere of fixed oxygen partial pressure of 0.0022 atm. If undoped or acceptor-doped, it would have taken no more than a few hundreds of seconds, see Fig. 4.1. This usually sluggish kinetics may be called the kinetic anomaly of donor-doped BaTiO\textsubscript{3}. Not surprisingly, the chemical diffusivity data are extremely sparse for donor-doped case. Only two data sets are found in the literature, one by Wernicke on La-doped and the other by Nowotny and Rekas on Nb-doped BaTiO\textsubscript{3} both only against temperature in fixed $P_{O_2}$ atmospheres (0.32 and 0.0022 atm, respectively).

A recent study shows that compared to that of the undoped counterpart in Figs. 4.1 that is usual, the relaxation behavior of donor-doped BaTiO\textsubscript{3} appears unusual depending on the oxygen activity.

It is brought back to the reader’s attention that in Fig. 2.6(c), the conductivity for the specimen denoted as $V_n$ is the equilibrium conductivity of La-doped BaTiO\textsubscript{3} (nominal composition $Ba_{0.85}La_{0.15}Ti_{0.975}O_3$), that has an average grain size of $0.86 \pm 0.03 \mu m$ and the bulk density of 96% of the the-
Fig. 4.7. Conductivity relaxation for the stepwise changes back and forth between the oxygen activities (in log a_O²⁻): (a) 0.01 → 0.59; (b) 1.89 → 2.49; (c) −7.91 → −8.61 and −8.66 → −7.91; (d) −8.65 → −9.43 and −9.44 → −9.53; (e) −9.41 → −10.20 and −10.21 → −9.42; (f) −13.02 → −13.83 and −13.80 → −13.05. Insets: exploded view of the first and faster relaxation. Note the change of kinetics from one-fold (a,b) to two-fold (c-e) to one-fold (f) as the mean oxygen activity decreases. Solid curves are the best fitted to Eq. 4.1 or Eq. 4.11 or Eq. 4.12 in the text. From Ref. 30.
Theoretical value. The corresponding defect structure is basically as shown in Fig. 2.3(d) and in more detail for the system in present concern, in Fig. 4.6: As $P_{O_2}$ decreases from 1 atm at the given temperature, the majority type of disorder shifts from $[La_{82}]_n=[V_{Ti}^n]$, through $[La_{82}]_n$, to $n=2[V_{O}]$.

Fig. 4.7(a)-(o) show sequentially the as-measured conductivity relaxation curves for stepwise changes back (reduction) and forth (oxidation) between the pre-fixed oxygen activities specified, as the (geometric) mean oxygen activity decreases. Clearly, the relaxation behaviors differ depending on the oxygen activity windows imposed or the mean oxygen activity. As the latter decreases from log $a_{o_2}$=0, the conductivity relaxes apparently with one relaxation time $(a,b)$, with two relaxation times $(c-e)$ and again with one relaxation time $(f)$. In other words, the kinetics varies from 1-fold to 2-fold to 1-fold with decreasing $a_{o_2}$. The 1-fold and 2-fold kinetics may be more clearly recognized from a plot of the relaxation curves $c(t)$ against log t, instead of t, see Fig. 4.6. It is noted in two-fold kinetics cases [Fig. 4.7(c)-(e)], that the two relaxation times differ by orders of magnitude.

4.2.2. Defect chemical interpretation

The two-fold relaxation is understood as follows: The nonmolecularity $n$ as well as oxygen nonstoichiometry $\delta$ of the system is presumed to be spatially homogeneous in the beginning. As soon as a different oxygen activity is imposed upon such a homogeneous system, a new redox equilibrium will be immediately established at the surface of the specimen via the redox reaction, Eq. 2.5, assuming the surface reaction is fast enough (Of course, this is not always the case though), and proceeds inward via chemical diffusion of component oxygen as is the case with the undoped or acceptor-doped $BaTiO_3$.

Now, we further assume that there also prevails initially the external equilibrium with respect to Ti-exchange (or Ba) between the system and a minority second phase or Eq. 2.6. The presence of the second phase has earlier been indicated upon shifting of the majority disorder types in the doped case[13], see Section 2. Such a second phase, however small it is, holds $a_{o_2}$ fixed. When the oxygen activity is suddenly changed to, say, a smaller value, while $a_{o_2}$ is fixed by the presence of the second phase, then due to the equilibrium condition Eqs. 2.4 and 2.6 (or $[V_{Ti}^n][V_O]=K_{o_2}$), a gradient of $[V_{Ti}^n]$ is established right at the surface where the surface reaction is again assumed to be fast enough. This gradient subsequently drives the chemical diffusion of, say, component Ti. The thermodynamic situation is depicted in Fig. 4.9[30].

It is well known that charge neutrality may break down at grain boundaries and surfaces. What is observed in the relaxation of Fig. 4.7, however, is a spatial average property of the specimen, not a local property and hence, the space charge effect may be neglected (i.e., the Debye length is assumed to be sufficiently small compared to the grain size.) The overall charge neutrality condition may then be written for the present case (see Eq. 2.23) as

$$n=[La_{82}]+2[V_O]-4[V_{Ti}]$$

(4.8)

Neglecting the mobility of the donor impurities $La_{82}$, temporal variation of the electronic carrier density $n$ may be written as

$$\frac{\partial n}{\partial t}=-2\frac{\partial [V_O]}{\partial t}+4\frac{\partial [V_{Ti}]}{\partial t}=-2V_{O}\frac{\partial J_{V_{O}}}{\partial t}+4V_{Ti}\frac{\partial J_{V_{Ti}}}{\partial t}$$

(4.9)

As the present system is essentially an electronic conduc-

![Fig. 4.8](image)

**Fig. 4.8.** Conductivity vs. time in a log scale. Note the one-fold and two-fold kinetics are clearly discerned, and if $\tau_{o_2}<<\tau_{o}$, the two-fold kinetics may turn like the one-fold one. From Ref. 30.

![Fig. 4.9](image)

**Fig. 4.9.** Thermodynamic situation and expected diffusion profiles of $[V_O]$ and $[V_{Ti}]$ with time upon an abrupt change of oxygen activity at the surface of a specimen $x=0$. Note that the surface is assumed to be always in equilibrium so that $[V_{Ti}^n][V_O]=const.$ and $D_{o_2}<<D_T$. From Ref. 30.
tor (electronic transference number, \( t_e \approx 1 \)) over the entire \( a_\text{ox} \), range of the present concern, as is clearly seen from Fig. 4.6, the local electroneutrality field will be negligible. Hence, diffusion of each type of ionic defects proceeds in the respective sublattices with no mutual coupling or

\[
\mathbf{J}_{\text{v}_{\text{O}}} = -D_{\text{O}} \nabla [V_{\text{O}}] \quad ; \quad \mathbf{J}_{\text{v}_{\text{T}}} = -D_{\text{T}} \nabla [V_{\text{T}}] \tag{4.10}
\]

where \( D_{\text{O}} \) and \( D_{\text{T}} \) are the chemical diffusivities of component O and T respectively.

Assuming these chemical diffusivities to be constant for small jumps of oxygen activity, one may obtain the solution to Eq. 4.9 associated with Eq. 4.10 for the initial and boundary conditions given in Fig. 4.9 as

\[
\frac{\sigma - \sigma_e}{\sigma - \sigma_e} = \frac{n - n_e}{n_0 - n_e} = \sum_{k=0}^{\infty} A_k \pi^2 \exp \left[ \frac{-2j+1}{4a^2} D_{\text{T}} t \right]
\]

with

\[
A_0 = \frac{2[V_{\text{O}}]_0 - [V_{\text{T}}]_0}{2[V_{\text{O}}]_0 - [V_{\text{O}}]_t - 4[V_{\text{T}}]_0 - [V_{\text{T}}]_t}; \tag{4.12}
\]

\[
A_n = \frac{-4j(D_{\text{T}})^2 [V_{\text{O}}]_t - [V_{\text{T}}]_t)}{2[V_{\text{O}}]_0 - [V_{\text{O}}]_t - 4[V_{\text{T}}]_0 - [V_{\text{T}}]_t}\tag{4.13}
\]

where \( \sigma, \sigma_e \) and \( \sigma_0 \) are the mean conductivity at time \( t \), the initial equilibrium conductivity at \( t=0 \) and the final equilibrium one as \( t \to \infty \), respectively, \( n, n_0 \) and \( n_e \) are the corresponding densities of carrier electrons, and "2a" the thickness of the present specimen that may be regarded as an infinite slab in the present case.

It is noted that this chapter 4.11 to evaluate the chemical diffusivities. In the one-fold kinetics region of \( \tau_0 \), all the relaxation data could be sufficiently precisely fitted to Eq. 4.11 with \( A_0 = 0 \), as depicted by the solid curves in Figs. 4.7(a) and (b), thus, indicating that the rate of surface reactions, Eqs. 4.1 and 4.2 are indeed fast enough compared with the chemical diffusion.

However, in the one-fold kinetics region of \( \tau_0 \), the surface reaction step has to be taken into account, as in the undoped or acceptor-doped cases, for a sufficient precision of the fitting. The relaxations are, thus, fitted (solid lines in Fig. 4.7(a-e)) to the conventional solution similar to Eq. 4.1, but in 1-dimension to evaluate \( D_{\text{O}} \) and the surface reaction rate constant \( k \) simultaneously.

Refer to the Figs. 4.10 and 4.11 to evaluate the chemical diffusivities. In the one-fold kinetics region of \( \tau_0 \), all the relaxation data could be sufficiently precisely fitted to Eq. 4.11 with \( A_0 = 0 \), as depicted by the solid curves in Figs. 4.7(a) and (b), thus, indicating that the rate of surface reactions, Eqs. 4.1 and 4.2 are indeed fast enough compared with the chemical diffusion.

All the results, \( D_{\text{O}} \), \( D_{\text{T}} \) and \( k \) (for oxygen exchange) as obtained in this way are compiled in Fig. 4.10. As is seen, \( D_{\text{O}} \) values are in the range of \( 1 - 10^{-5} \) cm²/s depending on oxygen activity. Upon comparison with the \( D_{\text{O}} \) values for the undoped and acceptor-doped in Fig. 4.4, one can recognize that these data are quite reasonable as the chemical diffusivity of oxygen in BaTiO₃. In addition, the surface reaction rate constants "k" are also comparable in magnitude as well as in trend with those for the undoped or acceptor-doped systems, see Fig. 4.2.

Here, however, one should note that the values for \( D_{\text{T}} \), being in the range of \( 10^{-3} \sim 10^{-5} \) cm²/s, seem too large in comparison with the two reported values for the chemical diffusivity of the cations in BaTiO₃, see Fig. 4.10. Remembering that in the evaluation of \( D_{\text{T}} \) via Eq. 4.11, the specimen thickness \( 2a \) (=1.2 mm) has been employed as the decisive diffusion length, it indicates that the decisive diffusion length should rather be the grain size than the specimen.
thickness.

Simply assuming that the specimen consists of spherical grains with a mean radius \(a_c\), Eq. 4.11 is modified to be:

\[
\frac{\sigma - \sigma_0}{\sigma_c - \sigma_0} = A_0 \frac{8}{\pi} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^{2}} \exp \left[ \frac{(2j+1)^{2} \pi^{2} D_{011}}{4a_{c}^{2}} \right] \\
+ A_{11} \frac{6}{\pi} \sum_{j=1}^{\infty} \frac{1}{j^{2}} \exp \left[ \frac{j^{2} \pi^{2} D_{111}}{a_{c}^{2}} \right] 
\]

Reanalyzing all the experimental data for the two-fold kinetics region and higher oxygen partial pressure region to this modified solution (solid lines in Fig. 4.7(a-e)), one obtains the results as shown in Fig. 4.11 along with all those literature data.\(^{31-32}\)

As is seen, the re-evaluated values are now in a satisfactory agreement with the reported chemical diffusivity values.\(^{31-32}\) It may, thus, be concluded that the two-fold kinetics is due to the chemical diffusion of oxygen and cation, say, Ti, the chemical diffusivities of which differ by ca. 8 orders of magnitude from each other.

In sum, what happens in the donor-doped \(\text{BaTiO}_3\) is that the oxygen sublattice has first been equilibrated with a decisive diffusion length of the overall specimen dimension, and the cation sublattice subsequently starts to re-equilibrate from grain surfaces, that is, with the grain size as the decisive diffusion length. Whether or not the two-fold kinetics is observed, seems to be determined by the combination of the relaxation times: If they are not much different, say, \(\tau_{O} = \tau_{Ti}\), or in other words, \(2a/\alpha \approx \sqrt{D_{0}/D_{111}}\), then it would not be possible to observe or discern the two-fold kinetics irrespective of the amplitude ratio \(R = A_{O}/A_{Ti}\) in Eq. 4.12. For the specimen in question, \(2a/\alpha = 10^3\) and \(\sqrt{D_{0}/D_{111}} = 10^4\), thus, observable.\(^{30}\) If \(\tau_{O} < \tau_{Ti}\), the two-fold kinetics should be observed in principle, but no matter what \(R\) value is, it would take too long to observe, or there would be little symptom of the cation sublattice relaxation in experimentally viable time. If \(R < 1\), on the other hand, the cation sublattice relaxation can hardly be detected experimentally, even if there occurs the relaxation. This may be the case of undoped or acceptor-doped \(\text{BaTiO}_3\) where the kinetics only

![Fig. 4.12. Thermodynamic factors \((\Theta\Delta l)\) for O (solid line) and Ti (dotted line) vs. oxygen activity as evaluated from the equilibrium defect structure of 1 m/o La-doped \(\text{BaTiO}_3\) in Fig. 4.6. From Ref. 30.](image)

![Fig. 4.13. Defect diffusivities of O and Ti vacancies, \(D_{O}\) and \(D_{Ti}\) vs. oxygen activity at 1200°C. The solid lines, the average values.](image)
appears one-fold and very fast.

4.3 Defect Diffusivities

Again according to Wagner,\(^2\) the chemical diffusivities in Eq. 4.10 may be written for an electronic conductor system \((t_o=1)\) as

\[
\hat{D}_0 = -D_0\left(\frac{\partial n_0}{\partial \ln[V_0]}\right) = -\frac{D_0}{2} \left(\frac{\partial \ln[\frac{V_0}{V_{\text{Ti}}}]}{\partial \ln[V_0]}\right)
\]

(4.13)

and

\[
\hat{D}_{\text{Ti}} = -D_{\text{Ti}}\left(\frac{\partial n_{\text{Ti}}}{\partial \ln[V_{\text{Ti}}]}\right) = \frac{D_{\text{Ti}}}{2} \left(\frac{\partial \ln[\frac{V_{\text{Ti}}}{V_{\text{Ti}}}]}{\partial \ln[V_{\text{Ti}}]}\right)
\]

(4.14)

due to the identity \(V_{\text{Ti}}:2V_{\mu_{0}}=V_{\mu_{\text{Ti}}:0}=0\) in the presence of the second phase. The quantities within the parentheses, the thermodynamic factors are nothing but the inverses of slopes of the curves for \([V_0]\) and \([V_{\text{Ti}}]\), respectively, in Fig. 4.6. They are graphically evaluated as in Fig. 4.12.

On the basis of Eqs. 4.13 and 4.14, one can, then, evaluate the defect-diffusivities of \(V_0\) and \(V_{\text{Ti}}\), \(D_0\) and \(D_{\text{Ti}}\), respectively. The results are finally as shown in Fig. 4.13. As is seen, each defect diffusivity turns out to be fairly flat against oxygen activity, as expected. Their values at 1200°C, \(D_0=1.4 \times 10^{-5}\) cm²/s; \(D_{\text{Ti}}=1.0 \times 10^{-7}\) cm²/s are quite reasonable in magnitude, upon comparison with the literature values if available. It should be pointed out that defect diffusivity of the cation vacancy has been evaluated for the very first time in BaTiO₃ and the like. Nevertheless, it is still yet to be elucidated which of \(V_{\text{Ti}}\) or \(V_{\text{Ba}}\) is in the majority, and which is more mobile whether doped or undoped. It has usually been believed that \(V_{\text{Ba}}\) is immobile relative to \(V_0\) for the energetic reason.\(^3\) A recent study,\(^4\) however, shows that the impurity diffusivities of Sr, that is replacing Ba, and Zr, that is replacing Ti, are comparable to each other.

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