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Thermodynamic Characterization of Ternary Compounds. I. The Case of Negligible Defect Association

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The complete thermodynamic specification of the state of a ternary compound requires control of one more experimental parameter than for the case of a binary compound. Two experimental approaches have been used: (a) equilibration with a fixed activity of one of the binary constituents of the ternary compound, and (b) the assumption of a fixed ratio of the two cationic species. It is shown that these two approaches are not equivalent, and that for the latter case, the activities of the binary constituents can vary widely with changes in the equilibrium nonmetal activity. For example, a ternary oxide with a fixed ratio of the two cationic components may be driven out of the single phase region by changes in ambient oxygen pressure, in effect transforming an initial case (b) to case (a), as defined above. $BaTiO_3$ is used as a specific example, and is discussed for the limiting case of negligible coulombic interaction between point defects.

Complete thermodynamic definition of a system consisting of a binary compound in equilibrium with one of its constituents, henceforth discussed in terms of a binary oxide in equilibrium with gaseous oxygen, requires the specification of two thermodynamic variables according to the phase rule. These are typically the temperature and the pressure, or fugacity, of the gaseous component, oxygen. In practice, it is not convenient to cover a wide range of oxygen pressures with a pure oxygen atmosphere, and a third component is added. This may be an inert diluent, such as argon or nitrogen, or a constituent in a gaseous equilibrium mixture, such as carbon in CO–CO_2 mixtures, or hydrogen in H_2–H_2O atmospheres. In the latter cases, very low oxygen fugacities can be achieved. The addition of the third component increases by one the number of variables that must be specified for complete thermodynamic characterization; the total pressure, usually one atmosphere, is the almost universal choice for the third parameter.

For the case of more complex oxides, the addition of each new component requires the specification of an additional variable. The situation for ternary compounds such as the spinels, AB_2O_4, and perovskites, ABO_3, has been rigorously derived by Schmalzried and Wagner (*1*, *2*), who used the activity of one of the constituent binary oxides as the additional variable, e.g., a_{AO} or $a_{B_2O_3}$ in a spinel, and a_{AO} or a_{BO_2} in a ternary oxide having the perovskite structure. (In cases where other ternary compounds exist in the pseudobinary system, it is of course necessary to restrict the binary oxide activity to values within the stability range of the desired phase.) This approach is often experimentally inconvenient, and may even be impractical if interdiffusion of the cationic constituents is very slow compared with the equilibration rates of other processes of interest. For these reasons, it has become increasingly common to assume that a fixed cationic composition suffices to serve as the additional defined variable. Thus, if both cationic species are sufficiently nonvolatile, the atomic ratio of the cations, A/B, whether known, or unknown but assumed constant, is considered adequate in addition to temperature, total pressure, and oxygen fugacity. It is obvious that this is not a

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completely adequate thermodynamic characterization over a range of temperature because the solubility of the binary constituents in the ternary compound will be a function of temperature. Thus, the composition of ABO_3, having a fixed A/B ratio, will correspond to that obtained by equilibration with a different a_{AO} at each temperature. Since the relationship between the composition of the ternary compound and the activity of its binary constituents is generally not known, this adds a degree of uncertainty to the precise thermodynamic state of the system. It does have the convenience, however, of preventing the concentrations of point defects related to a nonideal cation/cation ratio from being a function of temperature. Moreover, such a closed system, with invariant cationic composition, is the normal condition for practical application of complex oxides.

It has not been adequately appreciated that a fixed cation/cation ratio does not define the activities of the binary constituents even at constant temperature when the nonmetal activity is varied over a significant range. Thus, measurements of defect concentrations, electrical conductivity, or self-diffusion constants as a function of oxygen pressure at constant temperature and cation composition are equivalent to making the measurements with the ternary oxide in equilibrium with a different activity of binary constituent at each oxygen pressure. The effect can be very large for easily achievable experimental conditions, and can even drive the system to a phase boundary with subsequent separation of a second solid phase. This paper will explore these considerations for the limiting case of negligible defect interaction and association. The discussion will be in terms of a specific ternary oxide, $BaTiO_3$, which has been of particular interest to the author. The conclusions can be readily modified to fit other specific cases.

TiO_2-Rich $BaTiO_3$

According to the phase study of Rase and Roy on the BaO–TiO_2 system, there is a significant phase width of the TiO_2-rich side at elevated temperatures, e.g., about 1 mole % excess TiO_2 at 1400°C, while the stability range seems to be very narrow for BaO-rich compositions (*3*). Thus, we shall consider compositions initially in the TiO_2-rich single phase region. To maintain the perovskite structure of this phase, nonstoichiometric compositions must result in the presence of structural defects. It will be assumed that V''_{Ba} and $V_O^{\cdot\cdot}$ are the preferred defects for the incorporation of excess TiO_2, the alternative choices of $Ti_I^{\cdot\cdot\cdot\cdot}$ and O''_I or $Ti_{Ba}^{\cdot\cdot}$ and O''_I being less probable in the close-packed structure. Moreover, oxygen vacancies have been shown to be the oxygen-deficient defect in the closely related $SrTiO_3$ (*4*), and they appear to be the dominant ionic defect in oxygen deficient $BaTiO_3$ (*5–7*). In any case, the choice of defect model does not affect the general principles to be discussed. The assignment of double effective charges to both kinds of vacancy implies that both donor levels associated with oxygen vacancies lie above both acceptor levels associated with barium vacancies. This is supported by evidence that the oxygen vacancy levels in the similar compound $SrTiO_3$ are extremely close to the conduction band (*8*), and that oxygen vacancies in $BaTiO_3$ are either substantially (*6*), or entirely (*7*), doubly ionized at temperatures of 800°C and above. In accord with this assumed defect model, we can consider the incorporation of excess TiO_2 into an initially perfect $BaTiO_3$ lattice as an equilibrium reaction with an external phase of known TiO_2 activity, a_{TiO_2}, with the addition of one formula unit of new lattice sites:

$$TiO_2 \rightleftharpoons Ti_{Ti} + 2O_O + V''_{Ba} + V_O^{\cdot\cdot}. \quad (1)$$

For convenience, we shall assume that the oxygen pressure, P_{O_2}, has been adjusted to precise oxygen stoichiometry for the equilibrated crystal at the equilibration temperature. This is defined as the oxygen pressure such that the number of oxide ions, N_O, is given by

$$N_O = N_{Ba} + 2N_{Ti}, \quad (2)$$

i.e., the oxygen content exactly satisfies the ideal valence requirements of the cations present. This oxygen pressure will be represented by the symbol $P^0_{O_2}$. We can write a mass–action expression for (1)

$$[V''_{Ba}]\,[V^{\cdot\cdot}_O] = K_1 a_{TiO_2} \qquad (3)$$

where the brackets denote the activity of the enclosed species. We shall assume ideal solution behavior such that activities and concentrations of point defects are synonymous. For ideally pure material, the only source of electrons and holes at $P^0_{O_2}$ is by intrinsic ionization across the band gap, which is about 3.1 eV for $BaTiO_3$ (*6*). We shall assume that the concentrations of electronic defects so formed are negligible compared with the concentrations of ionic defects created by the excess TiO_2 according to (1). Moreover, we shall assume that ionic point defects related to any intrinsic ionic disorder, i.e., Frenkel defects of any of the three atomic species, or Schottky disorder, also can be neglected by comparison. This is reasonable in view of the unfavorable energetics for the intrinsic formation of ionic defects having two or more formal charges, especially in a close-packed structure. Thus, at precise oxygen stoichiometry, Eq. (1) is the only significant source of defects and

$$[V''_{Ba}] = [V^{\cdot\cdot}_O] = K_1^{1/2} a_{TiO_2}^{1/2} \qquad (\text{for } P_{O_2} = P^0_{O_2}). \qquad (4)$$

The concentrations of these defects under these experimental conditions will be symbolized by $[V''_{Ba}]_1$ and $[V^{\cdot\cdot}_O]_1$. Eq. (4) also can be considered to be an approximate expression of the condition of charge neutrality.

The permissable range of a_{TiO_2} is limited because of the intrusion of other phases. According to the phase diagram of Rase and Roy (*3*), $BaTiO_3$ at the TiO_2-rich phase boundary is in equilibrium with a liquid phase having $a_{TiO_2} < 1$ for temperatures above 1322° C, while at lower temperatures $BaTi_2O_5$ (1322–1210° C) and $BaTi_3O_7$ (<1210° C) are the phases of next higher TiO_2 content. We shall restrict our attention to temperatures below 1210° C, where $BaTi_3O_7$ is the adjacent phase of higher TiO_2 content. Thus, the region of interest could be treated as the pseudo-binary system $BaTi_3O_7$–$BaTiO_3$; however, for the sake of simplicity, we shall treat it as a BaO–TiO_2 system with a limited range of activities of the binary constituents.

The Oxygen Deficient Region

Let us consider the preparation of a single-phase sample of $BaTiO_3$ having an accurately known cation content corresponding to $Ba/Ti < 1$. This will be thermodynamically equivalent to equilibration of the sample with a known a_{TiO_2} at some specified temperature, followed by isolation of the sample from the source of TiO_2. The sample and its ambient oxygen pressure may then be treated as a closed system. If this hypothetical process is carried out near the value of $P^0_{O_2}$ appropriate to the equilibration temperature, the concentrations of barium and oxygen vacancies will be defined by Eq. (4).

If the sample is now equilibrated with lower oxygen pressures, $P_{O_2} < P^0_{O_2}$, oxygen will be removed from the crystal, in this case with the formation of additional oxygen vacancies and free electrons (*6, 7*) according to the reaction

$$O_O \rightleftharpoons \tfrac{1}{2}O_2 + V^{\cdot\cdot}_O + 2e', \qquad (5)$$

which leads to the following mass–action expression

$$n^2[V^{\cdot\cdot}_O] = K_5 P_{O_2}^{-1/2} \qquad (6)$$

where $n \equiv [e']$. It has been assumed that the oxygen vacancies are completely (doubly) ionized at the equilibration temperature in accord with the observed behavior of $SrTiO_3$ (*4, 8*). At equilibrium, Eqs. (3) and (6) must be obeyed simultaneously, the former being rearranged for convenience to

$$a_{TiO_2} = [V''_{Ba}]_1\,[V^{\cdot\cdot}_O]/K_1 \qquad (7)$$

there being no way to increase or decrease $[V''_{Ba}]$ in the closed system with a single solid phase.

Thus, at a given temperature, with $[V''_{Ba}]_1$ fixed in the closed system, a_{TiO_2} is proportional to the total $[V^{\cdot\cdot}_O]$. As long as the number of oxygen vacancies added by oxygen nonstoichiometry, Eq. (5), is small compared with those already present due to $Ba/Ti < 1$, then

$$[V^{\cdot\cdot}_O] \approx [V^{\cdot\cdot}_O]_1 \approx [V''_{Ba}]_1. \qquad (8)$$

$a_{\mathrm{TiO_2}}$ is then nearly independent of oxygen pressure, while electrons, and hence, the electronic conductivity, vary as

$$n = \left\{\frac{K_5}{[V_{\mathrm{O}}^{\cdot\cdot}]_1}\right\}^{1/2} P_{\mathrm{O_2}}^{-1/4} \tag{9}$$

Such a region is shown near $P^0_{\mathrm{O_2}}$ in Fig. 1, which is an idealized defect diagram for this system. Fig. 1 has been drawn to fit an arbitrary set of equilibrium constants, and the extreme range of $P_{\mathrm{O_2}}$ shown is experimentally unrealistic; however, for various other compounds, the experimentally accessible range can correspond to various parts of this diagram with a displaced $P_{\mathrm{O_2}}$ scale. Once the added oxygen vacancies make a significant contribution to the total, however, the situation changes drastically. In the $BaTiO_3$ (*6*, *7*) and $SrTiO_3$ (*4*, *9*) systems, the added oxygen vacancies completely dominate the total defect concentration at sufficiently low $P_{\mathrm{O_2}}$ as evidenced by the proportionality of the equilibrium conductivity to $P_{\mathrm{O_2}}^{-1/6}$. This dependence is typical of a new condition of charge neutrality.

$$n = 2[V_{\mathrm{O}}^{\cdot\cdot}] \gg [V_{\mathrm{O}}^{\cdot\cdot}]_1 \tag{10}$$

which with (6) gives

$$n = (2K_5)^{1/3} P_{\mathrm{O_2}}^{-1/6}. \tag{11}$$

Comparison of Eqs. (7), (10), and (11) shows that n, $[V_{\mathrm{O}}^{\cdot\cdot}]$, and $a_{\mathrm{TiO_2}}$ all have the same functional dependence on $P_{\mathrm{O_2}}$ in this region, as shown in Fig. 1. With the concentration of barium vacancies frozen at $[V''_{\mathrm{Ba}}]_1$ in the closed system, it is clearly feasible to increase $a_{\mathrm{TiO_2}}$ by reduction of $P_{\mathrm{O_2}}$ until the phase boundary is reached. As long as the $BaTiO_3$ phase persists, $a_{\mathrm{TiO_2}}$ cannot increase beyond the value defined by the phase boundary, $a^0_{\mathrm{TiO_2}}$, and continued reduction of $P_{\mathrm{O_2}}$ will result in the separation of the phase of next higher TiO_2 content, which is $BaTi_3O_7$ below 1210° C according to Rase and Roy (*3*).

In principle, $a^0_{\mathrm{TiO_2}}$ may also be a function of $P_{\mathrm{O_2}}$, and hence of the initial effective equilibrium $a_{\mathrm{TiO_2}}$ at $P^0_{\mathrm{O_2}}$, since the initial $a_{\mathrm{TiO_2}}$ will determine how low a $P_{\mathrm{O_2}}$ is required to push $a_{\mathrm{TiO_2}}$ the remaining distance to the phase boundary. This is presumably a small effect, reflecting in essence a greater tolerance of one of the solid phases for oxygen deficiency, and it will be ignored in the following discussion. It will be understood that $a^0_{\mathrm{TiO_2}}$ refers to the

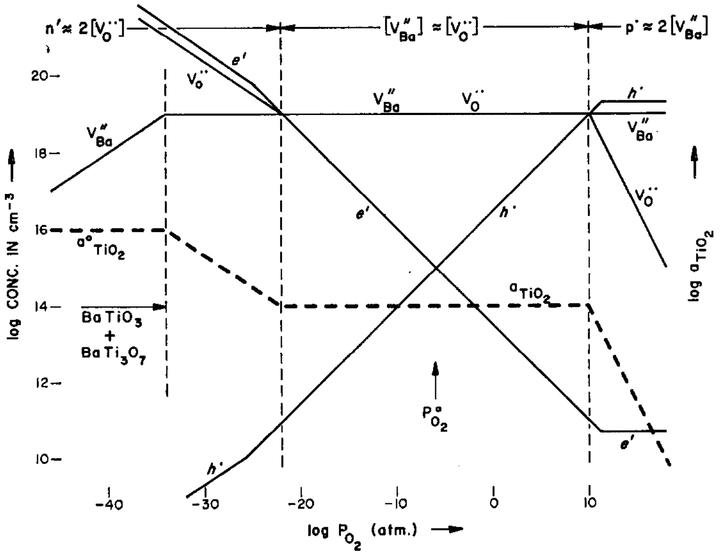

FIG. 1. Idealized defect diagram for TiO_2-rich $BaTiO_3$ with: $[V''_{\mathrm{Ba}}]_1 = [V_{\mathrm{O}}^{\cdot\cdot}]_1 = 10^{19}\ \mathrm{cm}^{-3}$; $K_i = 10^{30}\ \mathrm{cm}^{-6}$; $P^0_{\mathrm{O_2}} = 10^{-6}$ atm; arbitrary units for $a_{\mathrm{TiO_2}}$.

value at the phase boundary for the P_{O_2} appropriate for the particular starting composition in question.

The formation of $BaTi_3O_7$ from $BaTiO_3$ with the disappearance of barium and oxygen vacancies from the $BaTiO_3$ phase can be written as

$$3BaTiO_3 + 2V''_{Ba} + 2V^{\cdot\cdot}_O \rightleftharpoons BaTi_3O_7 + 2Ba_{Ba} + 2O_O. \quad (12)$$

Addition of this to twice the oxygen removal reaction, Eq. (5), gives

$$2V''_{Ba} + 3BaTiO_3 \rightleftharpoons BaTi_3O_7 + 2Ba_{Ba} + O_2 + 4e', \quad (13)$$

where the two solid phases are in equilibrium with the same $a_{TiO_2} = a^0_{TiO_2}$. The mass–action expression for this is

$$\frac{n^4}{[V''_{Ba}]^2} = K_{13} P_{O_2}^{-1}. \quad (14)$$

Combination of Eqs. (3), (10), and (14) leads to

$$n = (K_1 a^0_{TiO_2})^{1/3} (4K_{13})^{1/6} P_{O_2}^{-1/6} \quad (15)$$

$$[V^{\cdot\cdot}_O] = \tfrac{1}{2}(K_1 a^0_{TiO_2})^{1/3} (4K_{13})^{1/6} P_{O_2}^{-1/6}. \quad (16)$$

$$[V''_{Ba}] = \frac{2(K_1 a^0_{TiO_2})^{2/3}}{(4K_{13})^{1/6}} P_{O_2}^{1/6}. \quad (17)$$

Thus, n, the related electronic conductivity, and $V^{\cdot\cdot}_O$ continue to rise with decreasing P_{O_2} as $P_{O_2}^{-1/6}$, while V''_{Ba} now begins to decrease as $P_{O_2}^{1/6}$ and V''_{Ba} are consumed by the separation of the higher titanate.

It appears that the temperature dependences of the defect concentrations may have been changed by passage into the TiO_2-saturation regime. Eq. (11) indicates that prior to saturation, the temperature dependence of the electron concentration should be that of $K_5^{1/3}$, while Eq. (15) indicates that the temperature dependence will be that of $(K_1 K_{13}^{1/2} a^0_{TiO_2})^{1/3}$ in the saturation region. The mass–action expression for Eq. (12), the separation of $BaTi_3O_7$, can be expressed as

$$1/[V''_{Ba}]^2 [V^{\cdot\cdot}_O]^2 = K_{12} \quad (18)$$

and comparison with (3) shows that

$$K_{12} = 1/(K_1 a^0_{iTO_2})^2. \quad (19)$$

Also since Eq. (13) was obtained by the sum of (12) with twice (5),

$$K_{13} = K_5^2 K_{12}. \quad (20)$$

Thus, we can write the temperature dependence of n in the saturation region as

$$(K_1 K_{13}^{1/2} a^0_{TiO_2})^{1/3} = (K_1 K_5 K_{12}^{1/2} a^0_{TiO_2})^{1/3}. \quad (21)$$

By combination with (19), the right-hand side of (21) reduces to $K_5^{1/3}$, which is the same as the temperature dependence prior to saturation. Thus, n and $[V^{\cdot\cdot}_O]$ have the same P_{O_2} and temperature dependences before and after saturation. On the other hand, $[V''_{Ba}]$ has clearly changed from temperature independent to temperature dependent as we cross into the two phase region.

The major significance of these concepts is that if the original composition of a sample is such that the effective activity of one of the binary components near $P^0_{O_2}$ is within an order of magnitude of the saturation value at the experimental temperature, *and if the corresponding defects are unassociated,* the system will almost certainly be driven to the phase boundary with subsequent precipitation of a second solid phase whenever a significant region where $n \propto P_{O_2}^{-1/6}$ has been traversed with decreasing P_{O_2}. Of course, all of these considerations assume that nucleation and separation of the second phase occur within a reasonable time interval.

The Oxygen Excess Region

For the region $P_{O_2} > P^0_{O_2}$, the most favorable mechanism for the incorporation of a stoichiometric excess of oxygen should be the filling of some of the $V^{\cdot\cdot}_O$ which are available because of the TiO_2-excess composition (7)

$$V^{\cdot\cdot}_O + \tfrac{1}{2}O_2 \rightleftharpoons O_O + 2h^{\cdot} \quad (22)$$

for which the mass-action expression is

$$\frac{p^2}{[V^{\cdot\cdot}_O]} = K_{22} P_{O_2}^{1/2} \quad (23)$$

where $p \equiv [h^{\cdot}]$. As long as an insignificant portion of the preexisting $V^{\cdot\cdot}_O$ is filled, Eq. (4) remains valid, and

$$p = \{K_{22}[V^{\cdot\cdot}_O]_1\}^{1/2} P_{O_2}^{1/4}. \quad (24)$$

Such a region has been observed near $P_{O_2} = 1$ atm in $BaTiO_3$ by measurement of the electrical conductivity (*6*, *7*), and is shown in Fig. 1. If a significant proportion of the $V_O^{\cdot\cdot}$ has been filled, then both p and $[V_O^{\cdot\cdot}]$ become dependent on P_{O_2}. As essentially all of the $V_O^{\cdot\cdot}$ have been filled, p must eventually level off at a value

$$p \approx 2[V_O^{\cdot\cdot}]_1. \qquad (25)$$

Eq. (23) shows that at higher P_{O_2}, $[V_O^{\cdot\cdot}]$ must drop off as

$$[V_O^{\cdot\cdot}] = \frac{4[V_O^{\cdot\cdot}]_1^2}{K_{22}} P_{O_2}^{-1/2}. \qquad (26)$$

Such a region has not been observed with $BaTiO_3$ for P_{O_2} up to 1 atm. Since the material studied so far has had a substantial excess of TiO_2, $[V_O^{\cdot\cdot}]_1$ should be large enough to accommodate additional oxygen up to extremely high P_{O_2}.

If the situation corresponding to Eqs. (25) and (26) were to be reached, the decrease in $[V_O^{\cdot\cdot}]$, while $[V_{Ba}'']$ holds constant at $[V_{Ba}'']_1$ in the closed system, would result in a parallel decrease in a_{TiO_2}, in accord with Eq. (7). In this region, an increasing P_{O_2} rapidly drives the system toward compositions achievable by equilibration with very low values of a_{TiO_2}. Our treatment does not extend to a BaO-rich situation, with the appropriate defects for that case becoming of importance, but ultimately this must occur. Likewise, we have not permitted any other mechanism of oxygen incorporation. In principle, interstitial incorporation, accommodation on new lattice sites with the formation of *both* barium and titanium vacancies, or with movement of barium to titanium sites, will become important and p can begin to rise with increasing P_{O_2} again.

$$\tfrac{1}{2}O_2 \rightleftharpoons O_I'' + 2h^{\cdot} \qquad (27)$$

$$\tfrac{3}{2}O_2 \rightleftharpoons 3O_O + V_{Ti}'''' + V_{Ba}'' + 6h^{\cdot} \qquad (28)$$

$$\tfrac{3}{2}O_2 \rightleftharpoons 3O_O + Ba_{Ti}'' + 2V_{Ba}'' + 6h^{\cdot}. \qquad (29)$$

Actually, these two points are related. As a_{TiO_2} decreases, a_{BaO} increases, and the concentration of O_I'' (or V_{Ti}'''', or Ba_{Ti}'') must increase until it takes over the approximate condition of charge neutrality and allows p to rise with it with increasing P_{O_2}. At some point, a_{BaO} will reach another phase boundary, and Ba_2TiO_4 will separate out. These do not seem to be practical considerations as long as we start with TiO_2-rich $BaTiO_3$, and stay in the range $P_{O_2} \lesssim 1$ atm.

The Case of Predominant Electronic Disorder

We have assumed that the combination of relatively wide band gap and significant deviation from the ideal cation–cation stoichiometry means that electronic defects are negligible compared with ionic defects near $P_{O_2}^0$. In other words, Eq. (4) adequately expresses electrical neutrality in that region. This may not always be the case. If the band gap is sufficiently small, and if compositions are restricted to those having nearly ideal cation–cation stoichiometry, then the predominant disorder near $P_{O_2}^0$ may arise from intrinsic ionization

$$\text{nil} \rightleftharpoons e' + h^{\cdot} \qquad (30)$$

for which the mass action expression is

$$np = K_i. \qquad (31)$$

Under the stated conditions, the condition of charge neutrality near $P_{O_2}^0$ can be approximated by

$$n \approx p \approx K_i^{1/2}. \qquad (32)$$

Such a situation may be achievable with $BaTiO_3$ in the limit of ideal purity. This means that these defects will be independent of P_{O_2} near $P_{O_2}^0$, but, according to Eq. (6), $[V_O^{\cdot\cdot}]$ will vary as

$$[V_O^{\cdot\cdot}] = \frac{K_5}{K_i} P_{O_2}^{-1/2} \qquad (33)$$

and a_{TiO_2} will have a similar dependence according to Eq. (7). An idealized defect diagram for this situation is shown in Fig. 2. Once the added $V_O^{\cdot\cdot}$ become dominant and the approximate expression of charge neutrality changes to Eq. (10), the two types of systems have the same functional dependences. In Fig. 2, we have not introduced any mechanism for the incorporation of excess oxygen other

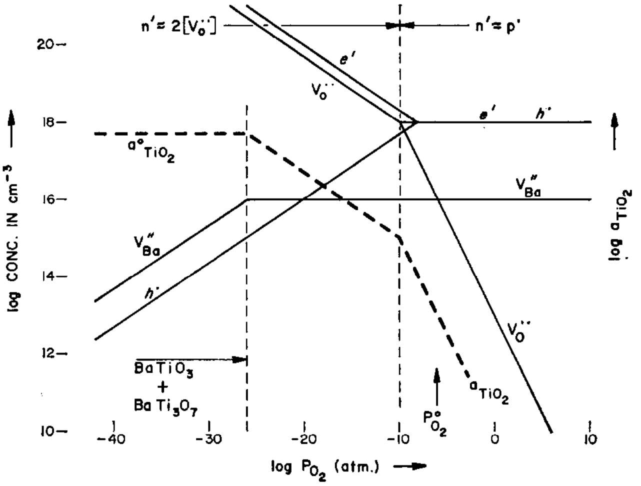

FIG. 2. Similar to Fig. 1, except that electronic defects predominate at $P_{O_2}^0$. $[V_{Ba}'']_l = [V_O^{\cdot\cdot}]_l = 10^{16}$ cm^{-3}; $K_i = 10^{36}$ cm^{-6}; $P_{O_2}^0 = 10^{-6}$ atm.

than the filling of compositionally related $V_O^{\cdot\cdot}$. An important feature of this situation with dominant electronic disorder is that a_{TiO_2} is nowhere independent of P_{O_2} within the BaTiO$_3$ single phase region. The very rapid decrease of a_{TiO_2} with increasing P_{O_2} above $P_{O_2}^0$ should lead very quickly to a phase boundary. It is also possible that the TiO$_2$-rich phase boundary will be reached before [V$_O^{\cdot\cdot}$] becomes significant compared with n. The range of P_{O_2} over which the single solid phase region is stable clearly depends on whether the predominant disorder at $P_{O_2}^0$ is electronic or ionic. These considerations will be particularly important for ternary compounds having relatively narrow band gaps.

Discussion

There are two possible experimental approaches based on Eq. (3), and the choice which has been made may not be obvious even to the investigator. For closed systems, as discussed here, where the A/B cation ratio is fixed in the solid system, the activities of the constituent binary components must adjust to the equilibrium P_{O_2} insofar as the concentration of one of the defects characteristic of A–B nonstoichiometry is affected. This adjustment must continue until a phase boundary is reached, after which further change of P_{O_2} in the same direction will result in the separation of an additional phase, and the related reduction of the complementary ionic defect, e.g., V_{Ba}'' in the case of extraction of oxygen from TiO$_2$-rich BaTiO$_3$.

For closed systems involving close-packed structures, such as oxides having the perovskite structure, the addition of excess oxygen ($P_{O_2} > P_{O_2}^0$) may encounter mechanistic difficulties when the A/B stoichiometry is nearly ideal. Thus, the $V_O^{\cdot\cdot}$ which results from excess TiO$_2$ in BaTiO$_3$, or whatever set of defects results from A/B nonstoichiometry, furnish an energetically favorable mechanism for oxygen incorporation as discussed above. Once that supply is exhausted, however, the alternative mechanisms are rather unappealing since they involve unfavorable defects, such as interstitial oxygen or titanium vacancies, or cations on the wrong sublattice, as shown in Eqs. (27–29). This may result in electronic conductivity that is independent of P_{O_2} in the high pressure range, such as shown in Figs. 1 and 2, while $[O_I'']$, $[V_{Ti}'''']$, or $[Ba_{Ti}'']$ are increasing with P_{O_2} toward significant values so that Eqs. (27), (28), or (29) can make significant contributions. At that point, the conductivity can rise again with P_{O_2}, but the temperature dependence should be large, reflecting the unfavorable enthalpy of the new reaction scheme. In view of the rapid drop in

a_{TiO_2} in the high P_{O_2} region, it is entirely possible that the next phase boundary will be reached before such reactions come into play. The separation of a new phase, such as Ba_2TiO_4 from $BaTiO_3$, in itself offers an attractive mechanism for the incorporation of excess oxygen

$$BaTiO_3 + \tfrac{1}{2}O_2 \rightleftharpoons Ba_2TiO_4 + V''_{Ba} + 2h^{\bullet}, \quad (34)$$

where the defects refer to the $BaTiO_3$ phase.

The alternative experimental approach is the continuous equilibration of the compound with a fixed activity of one of the binary constituents, as discussed in detail by Schmalzried and Wagner (*1*, *2*). This is usually accomplished by equilibration with an adjacent, coexisting phase, and the system is thus maintained at the phase boundary. In principle, the system could be equilibrated with an activity in the single phase region, and this would avoid the move toward a phase boundary with changing P_{O_2}, insofar as the boundary itself is not strongly dependent on P_{O_2}. Referring to Fig. 1, this approach would eliminate the region at low P_{O_2}, where $[V_O^{\bullet\bullet}]$ and a_{TiO_2} are increasing with decreasing P_{O_2}, while $[V''_{Ba}]$ holds constant ($10^{-34} < P_{O_2} < 10^{-23}$ atm). The entire region where $n \approx 2[V_O^{\bullet\bullet}]$ would look like the region where $P_{O_2} < 10^{-34}$ atm in Fig. 1. Of course, changes to a phase involving different oxidation states of the constituents are always possible and readily occur even in binary compounds, e.g., the reduction of Fe_3O_4 to FeO.

A particularly important change occurs in the region of high P_{O_2}, where $p \approx 2[V''_{Ba}]$. Here the presence of an additional phase offers a mechanism for the incorporation of excess oxygen which does not involve unfavorable defects. This can be written alternatively as

$$TiO_2 + \tfrac{1}{2}O_2 \rightleftharpoons Ti_{Ti} + 3O_O + V''_{Ba} + 2h^{\bullet} \quad (35)$$

$$BaTi_3O_7 + O_2 \rightleftharpoons 3BaTiO_3 + 2V''_{Ba} + 4h^{\bullet}. \quad (36)$$

These reactions can be sustained by the migration of only V''_{Ba} and $h^{\bullet}$, and are thus kinetically quite feasible. For this situation the mechanistic problem for the incorporation of excess oxygen does not exist as long as sufficient equilibrating phase is present. Eqs. (35) and (36) represent the incorporation of a stoichiometric excess of oxygen in the $BaTiO_3$ phase by consumption of a TiO_2-rich phase, while Eq. (34) accomplished a similar result by separation of a BaO-rich phase.

If the extent of solid solubility of one of the binary constituents in a ternary compound is overestimated, it is possible that an attempt to prepare a single phase solid with fixed A/B ratio may result in a two-phase equilibrated system. The behavior may then be quite different from that expected. Both of the extensive studies on $BaTiO_3$ may fall into that category, since the ceramic samples prepared by Long and Blumenthal (*5*) were reported to have 2–6 mole% excess TiO_2 and probably lie outside the single phase region according to the phase study of Rase and Roy (which does not claim great accuracy in this regard), and the single crystal used by Eror and Smyth (*7*) was grown from a TiO_2-rich melt, and thus, may undergo some phase separation in the temperature range used for the equilibrium studies of defect chemistry.

Although this discussion indicates that n and $[V_O^{\bullet\bullet}]$ in the $BaTiO_3$ phase, for the closed-system case and for $P_{O_2} < P^0_{O_2}$, show no discontinuities or change in dependence on experimental parameters as the system crosses into the region of two solid phases, and hence give no apparent clue to the changed situation, there may be practical experimental consequences, particularly for polycrystalline samples. An obvious example would be the effect on transport properties, such as electrical conductivity or oxygen self-diffusion, of the precipitation of large amounts of the second phase in intergranular regions. Moreover, Eq. (17) shows that $[V''_{Ba}]$ does become a function of both P_{O_2} and temperature in the two-phase region, and this could directly influence barium self-diffusion or the diffusion of other large divalent cations present as impurities.

The entire discussion has been based on the attainment of complete thermodynamic equilibrium. In some cases, the diffusion of the necessary species to a precipitation site for the new phase, or the nucleation of a new solid phase, may be very slow, and the system may exist in a supersaturated state. In the case of

$BaTiO_3$, segregation of $BaTi_3O_7$ or Ba_2TiO_4 requires only a redistribution of V''_{Ba} and $V_O^{\cdot\cdot}$ and the structural transformation itself.

This analytical treatment has explicitly excluded the effects of defect association. Practically all of the published discussion of the defect chemistry of ternary compounds has assumed that such association is negligible, and the conclusions reached here are thus pertinent to those conditions. It has been pointed out that the experimental results obtained for $BaTiO_3$, namely, that there is a broad region at low P_{O_2} where $n \propto P_{O_2}^{-1/6}$, are inconsistent with the fact that the number of $V_O^{\cdot\cdot}$ added by oxygen nonstroichiometry is negligible compared with the number already present due to the excess TiO_2 compositions (*7*). The results can be consistently explained if V''_{Ba} and $V_O^{\cdot\cdot}$ are very strongly associated into neutral vacancy pairs under the experimental conditions. This suggests that defect association may be very important indeed for some systems (*10*), and the implications of that for the present discussion will be dealt with in a subsequent publication.

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