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Thermodynamic Characterization of Ternary Compounds. II. The Case of Extensive Defect Association

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The thermodynamic characterization of an isolated ternary compound having a fixed cationic content is extended to include the effects of association of multiply charged point defects. $BaTiO_3$ containing a stoichiometric excess of TiO_2 is again used as a specific example. Defect association can remove the commonality of defect types originating from different sources, e.g., from nonideal cation ratios and from changes in nonmetal activity. As a result, the strong dependence of cation activities on the nonmetal activity can be greatly reduced in certain cases, and the possibility that changes in nonmetal activity will drive the compound into a two-phase region may be decreased accordingly.

Introduction

A previous paper discussed the complete thermodynamic definition of the state of an isolated ternary oxide in equilibrium with an oxygen-containing atmosphere (*1*). The discussion was in terms of a specific compound, $BaTiO_3$, which has the close-packed perovskite structure, and which is believed to be able to dissolve a significant stoichiometric excess of TiO_2 with the accompanying formation of barium vacancies and oxygen vacancies, V_{Ba}'' and $V_O^{\cdot\cdot}$ (*1*, *2*). Coulombic interaction between these doubly charged point defects was neglected. The analysis will now be extended to cover the case of strong interaction of these defects with nearly complete association into neutral vacancy pairs. In the author's opinion, this is the more probable situation for this class of compounds, even at temperatures as high as 1200°C (*3*, *4*). The basic concepts derived for this specific example can be easily generalized to cover other ternary or higher compounds.

The definitions and symbolism will be the same as in the earlier paper, and we are again dealing with isolated samples of invariant cation content, i.e., fixed Ba/Ti in $BaTiO_3$, rather than the case of fixed cation activities as discussed by Schmalzried and Wagner (*5*, *6*). The former situation is more convenient and commonly used, and corresponds to actual technological application.

In the earlier paper it was shown that for the case of negligible defect association, the activities of the binary components of $BaTiO_3$, i.e., a_{BaO} and a_{TiO_2}, are functions of the oxygen partial pressure, P_{O_2}, because the same defects are involved in accommodating a nonideal Ba/Ti ratio and in adding or extracting oxygen from the crystalline lattice. Thus material with Ba/Ti < 1 can formally be viewed as having been prepared by equilibration with an external source of TiO_2 which is subsequently removed.

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

This reaction represents the loss of TiO_2, and the disappearance of the related lattice sites, from the TiO_2 phase, and the gain of TiO_2 by the $BaTiO_3$ phase where it is accommodated by an increase in the number of lattice sites in the proper stoichiometric ratio. In this equation, and in all subsequent such reaction equations, the conservation of mass (atomic species), charge, crystal structure (ratio of

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lattice sites), and electronic states has been maintained. It has been assumed throughout that the defect concentrations are small enough to make the approximation that the concentrations of normally occupied sites are constant, and they are therefore not explicitly included in the mass–action expressions.

In the oxygen deficient region, the oxygen extraction reaction can be written as

$$O_O \rightleftharpoons \tfrac{1}{2}O_2 + V_O^{\cdot\cdot} + 2e', \tag{2}$$

while, in the region of higher oxygen pressures, where the crystal contains a stoichiometric excess of oxygen, the oxygen addition reaction can be written as

$$\tfrac{1}{2}O_2 + V_O^{\cdot\cdot} \rightleftharpoons O_O + 2h^{\cdot}. \tag{3}$$

Equations (2) and (3) are, of course, linked by the reaction representing the intrinsic ionization of electrons across the band gap

$$\text{nil} \rightleftharpoons e' + h^{\cdot}. \tag{4}$$

In (3) the $V_O^{\cdot\cdot}$ resulting from the BaO-deficiency are viewed as the energetically most attractive sites for the addition of a stoichiometric excess of oxygen. The mass–action expression for (1) is

$$[V_{Ba}''][V_O^{\cdot\cdot}] = K_1 a_{TiO_2}. \tag{5}$$

Thus with $[V_{Ba}'']$ fixed in the isolated, single-phase sample, changes in $[V_O^{\cdot\cdot}]$ by means of reactions (2) and (3) must result in changes in a_{TiO_2}, particularly when the number of oxygen vacancies created or consumed by (2) and (3) are of similar or greater magnitude than those resulting from the BaO deficiency. In that case a_{TiO_2} can be rather quickly driven to a value corresponding to the next phase boundary whereupon a two phase mixture will result from further changes in P_{O_2}.

If we now introduce the hypothesis that the defects generated by Reaction (1) are electrostatically attracted to the extent of almost complete association into vacancy pairs under the equilibration condition, (1) should be rewritten as

$$TiO_2(s) \rightleftharpoons Ti_{Ti} + 2\,O_O + (V_{Ba}''V_O^{\cdot\cdot}), \tag{6}$$

$$[(V_{Ba}''V_O^{\cdot\cdot})] \equiv [C] = K_6 a_{TiO_2}, \tag{7}$$

where the parentheses indicate that the enclosed species are electrostatically bound to adjacent lattice sites.

The Oxygen Deficient Region

The concept of defect association does not alter the probability that Reaction (2) is the most likely oxygen extraction reaction (*4*, *7–9*). Now, however, this process does not have a defect species in common with the BaO deficiency and therefore there is no direct effect on a_{TiO_2}. The only interaction will be through a common ion effect on the $V_O^{\cdot\cdot}$ generated by oxygen deficiency with those resulting from dissociation of the vacancy pair.

$$(V_{Ba}''V_O^{\cdot\cdot}) \rightleftharpoons V_{Ba}'' + V_O^{\cdot\cdot}. \tag{8}$$

$$[V_{Ba}''][V_O^{\cdot\cdot}] = K_8[C]. \tag{9}$$

This will have a negligible effect on a_{TiO_2} as long as the degree of association is very high in the first place. In contrast with the case without defect association (*1*), there is no direct relationship between a_{TiO_2} and P_{O_2} on the oxygen deficient side of stoichiometry.

This analysis is summarized in an idealized defect diagram in Fig. 1 for an ideally pure sample of BaO deficient $BaTiO_3$, where $P_{O_2}^0$ is the oxygen pressure corresponding to exact metal–nonmetal stoichiometry. In the near stoichiometric region near $P_{O_2}^0$ it has been assumed that the dominant defect species arise from the dissociation of the defect complex, Reaction (8), and that the condition of charge neutrality can be approximated by

$$[V_{Ba}''] \approx [V_O^{\cdot\cdot}]. \tag{10}$$

For $P_{O_2} \ll P_{O_2}^0$, Reaction (2) becomes the major source of defects and the condition of charge neutrality changes to

$$n \approx 2[V_O^{\cdot\cdot}]. \tag{11}$$

Equations (9)–(11), combined with the mass action expression for Reaction (2), and that for intrinsic electronic disorder

$$np = K_4, \tag{12}$$

lead to the dependence of defect concentrations on P_{O_2} shown in Fig. 1 for oxygen deficient compositions, i.e., for $P_{O_2} < P_{O_2}^0$. a_{TiO_2} is independent of P_{O_2} in this region.

The region of very low P_{O_2}, where $n \propto P_{O_2}^{-1/6}$ has indeed been observed in studies of $BaTiO_3$ (*4*, *7*, *9*, *10*), even for samples known to be

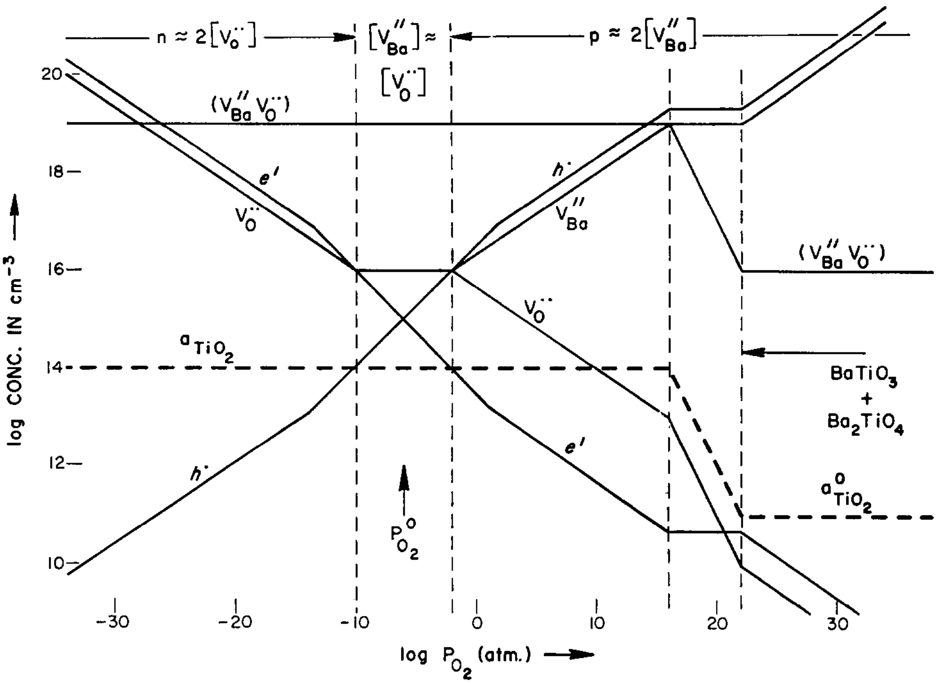

FIG. 1. Idealized defect diagram for TiO_2-rich $BaTiO_3$ with: $[(V_{Ba}'' V_O^{\cdot\cdot})] = 10^{19}\ cm^{-3}$; $[V_{Ba}''] = [V_O^{\cdot\cdot}] = 10^{16}\ cm^{-3}$, and $n = p = 10^{15}\ cm^{-3}$ both at $P_{O_2} = P_{O_2}^{o} = 10^{-6}$ atm; arbitrary units for a_{TiO_2}.

highly deficient in BaO (*4*, *7*, *10*). This dependence can arise only when Reaction (2) supplies more $V_O^{\cdot\cdot}$ than does the BaO deficiency, Reactions (1), or (6) and (8). From the known levels of oxygen deficiency (*9*, *11*), and the known or expected levels of BaO deficiency (*4*, *7*, *10*), *this condition could not be achieved without substantial association of the BaO-deficient defects.*

The oxygen-deficient region of Fig. 1 is in good agreement with experimental measurements of the equilibrium electrical conductivity of $BaTiO_3$ (*4*, *7*, *9*, *10*); however, the purity of real samples is such that charged impurity centers and their related defects appear to play a more important role than unassociated defects related to the BaO deficiency in the near stoichiometric region (*4*, *8*).

The Oxygen Excess Region

The addition of excess oxygen to interstitial sites, O_I'', or to new lattice sites with the corresponding formation of V_{Ba}'' and V_{Ti}'''', should be very unfavorable because of the lack of free space in the close-packed perovskite structure, and because of the high charge on the titanium vacancy. Thus, even though defect association would remove the free $V_O^{\cdot\cdot}$ which could accommodate extra oxygen according to Reaction (3), even the bound $V_O^{\cdot\cdot}$ related to BaO deficiency probably offers the most favorable mechanism in ideally pure $BaTiO_3$.

$$(V_{Ba}'' V_O^{\cdot\cdot}) + \tfrac{1}{2}O_2 \rightleftharpoons O_O + V_{Ba}'' + 2h^{\cdot}. \quad (13)$$

$$[V_{Ba}]p^2 = K_{13}[C]P_{O_2}^{1/2}. \quad (14)$$

In the near-stoichiometric region, Eq. (10) will still represent the approximate condition of charge neutrality, and an insignificant portion of the divacancy complex will be consumed. Under these conditions, $p \propto P_{O_2}^{1/4}$, as observed, and as shown in Fig. 1; although in actual samples, the presence of accidental acceptor impurities and related $V_O^{\cdot\cdot}$ appear to dominate this region (*4*). As Reaction (13) becomes the major source of defects, (10) can be replaced by

$$p \approx 2[V_{Ba}''], \quad (15)$$

and both of these defects will increase as $P_{O_2}^{1/6}$. If the BaO deficiency is large enough, however, as shown in Fig. 1, $[C]$ will still be essentially independent of P_{O_2}, and so will a_{TiO_2}, according to Eq. (7).

For sufficiently low BaO deficiency, or sufficiently high P_{O_2}, Reaction (13) could eventually consume practically all of the bound $V_O^{\cdot\cdot}$. At this point p and $[V_{Ba}'']$ would saturate with Eq. (15) still being valid. All of the pressure dependence of Eq. (14) would now have to be reflected in $[C]$, and with Eq. (7) we now have

$$a_{TiO_2} \propto [C] \propto P_{O_2}^{-1/2}. \qquad (16)$$

This is the only case so far which leads to a dependence of a_{TiO_2} on P_{O_2} and is shown in the next higher pressure region of Fig. 1. The P_{O_2} dependences in this region are, in fact, the same as expected for the case of negligible defect association when most of the $V_O^{\cdot\cdot}$ have been filled (1). If this condition could persist to high enough P_{O_2}, a significant change in the oxygen content could occur only by some new and less favorable mechanism, perhaps by the formation of O_I'', or V_{Ba}'' and V_{Ti}''''. The dependences shown in the next to highest region of P_{O_2} in Fig. 1 would then persist with increaing P_{O_2} until either $[O_I'']$ or $[V_{Ti}'''']$ approach the level of $[V_{Ba}'']$ and p. Then p and the new defect would begin to increase with P_{O_2}. In view of the concurrent sharp decline in a_{TiO_2}, however, it seems more likely that a phase boundary would be reached rather quickly with further increase in P_{O_2} with constant $a_{TiO_2} = a_{TiO_2}^0$, with subsequent separation of a lower titanate, such as Ba_2TiO_4 (1). This can be represented as

$$\tfrac{1}{2}O_2 + BaTiO_3 + Ba_{Ba} \rightleftharpoons Ba_2TiO_4 + V_{Ba}'' + 2h^{\cdot}, \qquad (17)$$

where the defects refer to the $BaTiO_3$ phase. As shown for the region of highest P_{O_2} in Fig. 1, $[V_{Ba}'']$ and p can then increase again with P_{O_2} with simultaneous transformation of $BaTiO_3$ into Ba_2TiO_4. While there is no indication that such a situation is attainable for $BaTiO_3$, it could be important in other complex oxides, particularly where there is a greater tendency for a stoichiometric excess of oxygen. This would be the case for oxides containing a cation which has a higher stable oxidation state.

Discussion

In general, one expects the same kinds of lattice defects to occur in a given crystal regardless of the driving force. They will be those defects which cause the least spatial and electrostatic distortion of the crystal as indicated by their enthalpies of formation. The defects may result from intrinsic disorder, aliovalent impurities, metal–nonmetal nonstoichiometry, or from nonideal cation ratios in compounds having more than one major cationic species. There is thus always the possibility of interconnection between these types of disorder. The first three types of disorder can occur in binary compounds and their interconnection is generally recognized. The fourth type of disorder is peculiar to compounds having a greater compositional complexity and its interconnection with the other three has frequently been neglected. That is a major point of these two papers. The defects are generated in different combinations, however, according to their source, e.g., in $BaTiO_3$ we appear to have V_{Ba}'' and $V_O^{\cdot\cdot}$ (and/or their associate) from nonideal cation ratios, $V_O^{\cdot\cdot}$ and e' from oxygen deficiency, and $V_O^{\cdot\cdot}$ due to acceptor impurities (4), and these combinations have differing tendencies to associate. Association creates a new and different defect species which may therefore have only an indirect interaction with the defects related to other types of disorder. This is the other major point.

The high degree of interaction in the absence of defect association was emphasized in the previous paper, where it was shown that it is quite likely that wide excursions in nonmetal activity either above or below $P_{O_2}^0$ can drive the system out of the single-phase region, even without considering the separation of compounds having one or more of the cations in a different oxidation state. The introduction of strong association for one set of defects, those related to a nonideal cation ratio in this paper, greatly reduces the amount of interaction. For the $BaTiO_3$ example used here, the effect of reducing P_{O_2} in the oxygen–deficient region then has only a trivial effect on the cation activities, while interaction occurs in the oxygen-excess region when the concentrations of the defects from both sources become comparable, just as in the case of negligible defect association.

The amount of defect association will depend on the defect charges, the crystal structure, the degree of ionicity, the polarizability of the structure and the surrounding atoms, the concentration of defects, and the temperature. All except the last two items are summed up in the enthalpy of association which appears in the mass action expression for the association reaction, e.g., for the reverse of Eq. (8), where the mass action constant in Eq. (9) can be related to the enthalpy of association, ΔH_a, as

$$\mathrm{K}_8 \propto e^{\Delta H_a/kT}. \tag{18}$$

As a very crude approximation, ΔH_a can be related to a coulombic energy

$$\Delta H_a = Z_1 Z_2 e^2/\varepsilon_s r, \tag{19}$$

where $Z_1 e$ and $Z_2 e$ are the charges on the two defects, r their separation, and the static dielectric constant ε_s sums up all of the polarization terms. An extensive body of information exists which indicates that ΔH_a for divalent impurity cations and cation vacancies in alkali halides, e.g., $\mathrm{Sr}_{\mathrm{Na}}^{\cdot}$ and V'_{Na} in NaCl, is about −0.5 eV (*12*, *13*), while there is enough evidence to suggest that ΔH_a for cation and anion vacancies in these crystals, e.g., $V_{\mathrm{Cl}}^{\cdot}$ and V'_{Na} in NaCl, is about −1 eV (*12*, *13*). The latter value is larger than the former because the defects are closer by a factor of $(2)^{1/2}$ and are true nearest neighbors with much less screening of their charges by intervening electron clouds, with a corresponding reduction in ε_s. The vacancy pair is the closer analog of the $(V''_{\mathrm{Ba}} V_{\mathrm{O}}^{\cdot\cdot})$ complex discussed in these papers since they both represent defects on adjacent lattice sites. Even when only one of the defects is doubly charged, the degree of association can be significant to quite high temperatures. It has been proposed that defect pairs of the type $(M_{\mathrm{Ni}}^{\cdot} V''_{\mathrm{Ni}})'$ make significant contributions to the diffusion of Al^{+3} (*14*) and Cr^{+3} (*15*) in NiO up to nearly 1800°. When we now consider association between two doubly charged defects it is clear from Eq. (19) that we can expect a substantial increase in ΔH_a. Neglecting changes in separation distance, and without knowing what to use for an effective ε_s in $\mathrm{BaTiO_3}$, it is not at all unlikely that $-\Delta H_a$ will exceed 2 eV for $(V''_{\mathrm{Ba}} V_{\mathrm{O}}^{\cdot\cdot})$, and that would be sufficient to insure a very high degree of association to temperatures well above 1000°.

In these papers, we have ignored the possible separation of a phase containing one of the atomic species in a different oxidation state, e.g., a phase containing Ti^{+3} at low $P_{\mathrm{O_2}}$. There is no experimental evidence for the formation of such compounds in the case of $\mathrm{BaTiO_3}$ for oxygen pressures between those achievable with CO–$\mathrm{CO_2}$ mixtures and $P_{\mathrm{O_2}} = 1$ atm. and for temperatures up to 1200°, but in principle such effects must become important at sufficiently low $P_{\mathrm{O_2}}$ with the ultimate separation of a phase containing lower valent titanium. This is the ternary analog of such familiar phenomena as the reduction of $\mathrm{Fe_3O_4}$ to FeO, or the oxidation of $\mathrm{Cu_2O}$ to CuO. The importance of such effects will depend on the chemistry of each particular system.

In cases where the cation–cation ratio is nearly ideal, or where the dissociation of the defect complex is sufficiently small, and where the band gap is sufficiently small, intrinsic electronic disorder may give the dominant charged defects in the near-stoichiometric region. This would result in only modest changes in the form of Fig. 1. The condition of charge neutrality would be $n \approx p$ instead of $[V''_{\mathrm{Ba}}] \approx [V_{\mathrm{O}}^{\cdot\cdot}]$ in the near-stoichiometric region and n and p would be independent of $P_{\mathrm{O_2}}$ in this region while, according to the mass action expressions for the oxygen extraction and addition reactions, $[V_{\mathrm{O}}^{\cdot\cdot}]$ and $[V''_{\mathrm{Ba}}]$ would vary as $P_{\mathrm{O_2}}^{-1/2}$ and $P_{\mathrm{O_2}}^{1/2}$, respectively. In other words the identity of the lines in the characteristic central inverted triangle near $P_{\mathrm{O_2}}^0$ in Fig. 1 would be reversed and the sides would be twice as steep. Outside of the near-stoichiometric region there would be no changes.

Finally, all discussion has been based on the ideally pure material; but, alas, such materials do not exist. In oxides in particular, the enthalpies of formation of the multiply charged ionic point defects are so high, as is the band gap, that the concentrations of intrinsic defects are generally small compared with presently achievable impurity levels. Thus the defect chemistry is dominated by these impurities and related charge compensating defects over some range of conditions centered on precise stoichiometry. In the case of $BaTiO_3$ of the highest available purity (about 100 ppm atomic of uncompensated acceptor impurities) only at the lowest P_{O_2} and highest temperature is the behavior independent of the impurity content (*4*). The presence of these impurities does not change the concepts discussed in these papers, however, and their effects are easily introduced.

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