DEFECT CHEMISTRY IN SOLID STATE ELECTROCHEMISTRY

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I. INTRODUCTION

Solid electrolytes and mixed ionic–electronic conductors (MIECs) have been known for quite some time, going back at least to Faraday's observations in the 1830s that lead fluoride when heated to red hot conducts electricity similar to platinum. Some 50 years later, Warburg described the migration of sodium through a glass and its precipitation on the glass surface when a direct current flowed through the glass. At the turn of the century, Nernst¹ discovered that the high ionic conductivity of doped zirconia was due to the transport of oxide ions,¹ while the unusually high ionic conductivity of the α -phase of silver iodide which exists above 420 K, and which is comparable with the best conducting liquid electrolytes, was found in 1914.²

These observations concerning ionic transport can be explained on the basis of defect chemistry and crystal structure of the solid materials. The ideal crystal is in fact an abstract concept that is used in crystallographic descriptions. The lattice of a real crystal always contains imperfections. A suitable classification of crystalline defects can be achieved by first considering point defects and then proceeding to one- and higher-dimensional defects. Point defects are atomic defects whose effects are limited only to their immediate surroundings. They exist in a state of complete thermodynamic equilibrium. Examples are ionic vacancies in the regular crystal lattice, or interstitial atoms or ions.

Besides, crystals often contain extended defects. Among these are dislocations, which are classified as linear or one-dimensional defects. Grain boundaries, chemical twinning, stacking faults, crystallographic shear planes, intergrowth structures, and surfaces are two-dimensional

TABLE 5.1
Solid Electrolytes

Point defect type		Positional disorder		Orientational disorder	
Dilute	Concentrated	Cation-disordered sublattice			
		Type I	Type II		
		Low T			
AgCl	ZrO ₂ -Y ₂ O ₃	α -AgI	LiAl ₅ O ₈	NaNO ₃	Li ₂ SO ₄
PbBr ₂	CaF ₂ -LaF ₃	RbAg ₄ I ₅		KNO ₃	Na ₂ SO ₄
LaF ₃	BaCeO ₃ -Re	β -alumina		NaBF ₄	K ₂ SO ₄
		High T			
		LiSO ₄			

defects. Finally, block structures, pentagonal column structures, infinitely adaptive structures, extended defect clusters, inclusions, or precipitates in the crystal lattice can be considered as three-dimensional defects. The concentrations of one- and higher-dimensional defects are not determined by thermodynamic equilibria. For the different kinds of defects, see also Chapter 3 of this handbook.

While certain preliminary ideas about the origin of ionic conduction in crystalline solids were derived from the crystal structure investigations of α -AgI by Strook,³ and relate to a molten sublattice, i.e., no distinction can be made between a regular Ag lattice site and an Ag on an interstitial site, our knowledge of point defects is based mainly on the work of Frenkel,⁴ Wagner and Schottky,⁵ Schottky,⁶ and Jost,⁷ and was developed primarily by studying electrical and optical properties.

A possible classification of solids where ionic conductivity plays an important role is given in Table 5.1. In contrast to the situation in solutions, ionic transport in solids is accompanied by an electronic counterpart. For solid electrolytes the ionic contribution to the total electrical conductivity is predominant. Other cases represent MIECs.

A similar classification can be made for MIECs. MIECs are dealt with extensively by Riess in Chapter 7 of this book.

Type I positional disorder occurs because the lattice offers a large excess of available lattice positions for the mobile ions. These sites need not all be positions of the same energy, and indeed, generally they are not. Consequently, in the disordered state of the crystal the distribution of the ions in question among the sites to which they have access is not necessarily completely random. The ordered state of such a compound may have essentially the same structure, but with an ordered arrangement of occupied and unoccupied sites. Alternatively, it may have a different structure in which the number of sites now equals the number of ions.

Type II positional disorder is encountered in compounds in which some of the ions occupy quite definite positions, with the disorder confined to the positions of some or all of the remaining ions. The randomness involves one or more sublattices rather than all the lattice sites. Thus, type II disorder can occur in spinels of formula AB₂O₄, in which the oxide ions occupy fixed lattice positions, and any disorder concerns the whereabouts of the A and B ions. It is possible for a crystal to be simultaneously disordered in both ways, an instance of this being the high-temperature phase of the compound Ag₃SI.

Concentrated defect compounds show high lattice disorder and usually strong interactions between the moving ions, and thus resemble cation-disordered sublattice conductors. However, a distinction between normal and interstitial positions in a disordered sublattice is meaningless from a defect chemical point of view.

Orientational disorder in ionic solids arises because a diatomic or polyatomic ion has available to it two or more distinguishable orientations in the crystal lattice. This kind of disorder is a fairly common occurrence, especially when the polyatomic ions are sufficiently symmetrical. If these ions are associated with monoatomic ions of opposite charge, the

situation simplifies in that the diatomic or polyatomic ions are to some extent protected from interference from ions of the same kind by the intervening shell of the monoatomic ions. Switching of diatomic or polyatomic ions from one orientation to another may induce local stress and hence facilitate the displacement of the monoatomic ion. A crystal can have positional disorder and at the same time orientational disorder of a polyatomic ion or molecule. Examples of this behavior are provided by lithium iodide monohydrate, and the high-temperature form of lithium sulfate.

While ionic conduction is mainly related to crystal structure, electronic conduction is determined by the electronic band gap, which depends more on the individual properties of the constituent ions. Thus in a series of compounds with comparable ionic conductivities, electronic conductivities can vary from virtually zero to quasimetallic. The first kind may find application as the solid electrolyte in a variety of solid state electrochemical devices, while the electrodes for these devices may be selected from the other.

The materials developed to date, for instance, for rechargeable solid state batteries, high-temperature fuel cells and electrolyzers, smart windows, and environmental gas sensors are numerous, and while many exhibit positional or orientational disorder, an overwhelming number conducts by virtue of point defects, and the defect chemistry of these materials is the focus of this chapter.

II. DEFECT CHEMISTRY OF BINARY AND TERNARY COMPOUNDS

Since the pioneering work of Frenkel, Schottky, Wagner, and Jost, a great number of studies, textbooks, and monographs have appeared which describe defect chemistry, dealing with equilibrium disorder in mainly binary ionic compounds.⁸⁻²³ In several of these references the one- and higher-dimensional defects mentioned before are being discussed in detail, while an excellent survey of positional and orientational disorder has been published by Parsonage and Staveley.²⁴

The defect chemistry of ternary compounds has also attracted widespread attention, and the more fundamental concepts were developed mainly in the 1960s and 1970s.^{8-10,17,25-34}

Since the field of solid state ionics was defined by Takahashi in the early 1960s, and the very first international meeting on the ever growing field of solid state ionics was held in Belgirate in 1972,³⁵ a great number of studies have appeared in which structural concepts and concepts of the defect chemistry of binary and ternary compounds have been applied in order to not only improve the electrical properties of existing materials, but also to guide solid state chemists and physicists and materials scientists in developing new materials. A selection of the literature is presented in References 36 to 59.

A. DEFECTS AND NONSTOICHIOMETRY IN BINARY COMPOUNDS

Point defects fall into two main categories: *intrinsic defects*, which are internal to the crystal in question, and *extrinsic defects*, which are created when an impurity atom or ion is inserted into the lattice. In, for instance, metal oxides containing transition metal ions, usually a component-dependent extrinsic disorder predominates.

The intrinsic defects fall into two main categories, i.e., Schottky disorder and Frenkel disorder. As these point defects do not change the overall composition, they are also referred to as *stoichiometric defects*. Their thermal generation will be exemplified for a metal oxide MO using the Kröger-Vink⁸ notation, and assuming that activities of point defects are equal to their concentrations. Hence, the law of mass action is applicable to these equilibria.

Schottky disorder:

with equilibrium constant

$$K_s = [V_M''] [V_O^{\bullet\bullet}] \quad (5.2)$$

Here, $(MO)_{\text{defect}}$ denotes a lattice unit at the surface of the crystal.

Frenkel disorder:

The equilibrium constant is

$$K_F = [M_i^{\bullet\bullet}] [V_M''] \quad (5.4)$$

Frenkel disorder usually occurs in the cation sublattice. It is less common to observe Frenkel disorder in the anion sublattice (*anti-Frenkel disorder*), and this is because anions are commonly larger than cations. An important exception to this generalization lies in the occurrence of anti-Frenkel disorder in fluorite-structured compounds, like alkaline earth halides (CaF_2 , SrF_2 , SrCl_2 , BaF_2), lead fluoride (PbF_2), and thorium, uranium, and zirconium oxides (ThO_2 , UO_2 , ZrO_2). One reason for this is that the anions have a lower electrical charge than the cations, while the other reason lies in the nature of the open structure of the fluorite lattice.

Anti-Frenkel disorder is represented by:

with equilibrium constant

$$K_{aF} = [O_i''] [V_O^{\bullet\bullet}] \quad (5.6)$$

The temperature dependence of the number of Schottky defects is given by

$$[V_M''] = [V_O^{\bullet\bullet}] = n_s = N \exp \left(-\Delta H_f / 2kT \right) \quad (5.7)$$

where n_s is the number of one of the intrinsic Schottky defects per cubic meter at temperature T in a crystal with N cations and N anions per cubic meter. ΔH_f is the enthalpy required to form a set of vacancies. Equation (5.7) has been derived taking into account only variations in the configurational entropy. In the simplest case of the Einstein approximation for the limiting case of Dulong–Petit behavior, a crystal with N lattice atoms is considered to be a system of $3N$ oscillators that all vibrate with the same frequency ν_0 . From the partition function of this ensemble of oscillators, that part of the Gibbs free energy which arises from the crystal vibrations can be used to calculate the change in the vibrational frequencies, accompanying the introduction of point defects. The corresponding entropy change appears as a pre-exponential factor in Equation (5.7) and does not influence the temperature dependence of the concentration of point defects.

For the alkali and lead halides, a simple empirical relation exists between the formation enthalpy of Schottky defects and the melting temperature T_m ,¹³ i.e.,

$$\Delta H_f(eV) = 2.14 \times 10^{-3} T_m(K) \quad (5.8)$$

For oxides, no such simple empirical relation has been reported.

The concentration of the intrinsic point defects can be influenced by aliovalent impurity doping. Assuming that only ionic point defect concentrations are affected, the following lattice reactions exemplify the formation of extrinsic disorder by substitution in MO, e.g., MF_2 in MO

and Me_2O in MO

In general, in compounds with k components at constant temperature and pressure, the concentrations of point defects present in thermodynamic equilibrium are fixed by $k-1$ component activities or the related chemical potentials.

For the simple metal halides and metal oxides, at P and T fixed, usually the halogen or oxygen partial pressure is used, because this parameter can easily be varied. The dependence of the defect concentrations on component activities is determined by the predominating intrinsic defect structure and is analyzed using point defect thermodynamics.

1. Metal Halides

In the metal halides to be discussed here, Frenkel disorder predominates. Equilibrium with an X_2 containing ambient can be established according to

and

with

$$K_a = \frac{[V_M'] [h^\bullet]}{p_{X_2}^{\frac{1}{2}}} \quad (5.13)$$

and

$$K_b = [M_i^\bullet] [e'] p_{X_2}^{\frac{1}{2}} \quad (5.14)$$

the respective equilibrium constants. The intrinsic ionic and electronic disorder reactions are

and

where O denotes the perfect lattice.

The equilibrium constants are

$$K_F = [M_i'] [V_M'] \quad (5.17)$$

and

$$K_i = [e'] [h'] \quad (5.18)$$

Heyne⁶⁰ has shown that the electronic band gap of solid electrolytes should always be larger than $\frac{T}{300}$ (eV).

For $M_{1+x}X$ the mass balance equation reads

$$[M_M^x] + [M_i'] + [e'] = 1 + x \quad (5.19)$$

$$(e' \equiv M_M')$$

while for $M_{1-x}X$ the equation is

$$[X_x^x] + [X_i'] + [h'] = 1 \quad (5.20)$$

$$(h' \equiv X_x')$$

The site balance equations are

$$[M_M^x] + [V_M'] + [e'] = 1 \quad (5.21)$$

and

$$[X_x^x] + [h'] = 1 \quad (5.22)$$

From Equations (5.19) and (5.21) one obtains for x

$$x = [M_i'] - [V_M'] \quad (5.23)$$

If $P_{X_2}(0)$ represents the partial halogen pressure in equilibrium with stoichiometric MX, the following composition conditions can be distinguished:

- (i) $x > 0$, $[M_i^{\bullet}] > [V_M']$ for $P_{X_2} < P_{X_2}(0)$
- (ii) $x = 0$, $[M_i^{\bullet}] = [V_M']$ for $P_{X_2} = P_{X_2}(0)$
- (iii) $x < 0$, $[M_i^{\bullet}] < [V_M']$ for $P_{X_2} < P_{X_2}(0)$

From the equations for K_a , K_F and x , one obtains for the relation between the relative partial halogen pressure $P_{X_2}/P_{X_2}(0)$ and the deviation from stoichiometry the relation

$$\left(\frac{P_{X_2}}{P_{X_2}(0)}\right)^{\frac{1}{2}} = \left[-\frac{x}{2K_F^{\frac{1}{2}}} + \left(\frac{x^2}{4K_F} + 1\right)^{\frac{1}{2}} \right] \frac{[h^{\bullet}]}{[h^{\bullet}(0)]} \quad (5.24)$$

With $[h^{\bullet}(0)] = K_i^{1/2}$, K_i , and $[e'] - [h^{\bullet}] = x$, as well as the conditions $K_F^{1/2} \gg K_i^{1/2}$ and $x \ll K_F^{1/2}$, Equation (5.24) reduces to

$$\log \frac{P_{X_2}}{P_{X_2}(0)} = 2 \log x / -\log K_i \quad (5.25)$$

for $x < 0$ and $|x| \gg K_i^{1/2}$.

For given P_{X_2} the deviation from stoichiometry increases with increasing values for K_i . The relation between

$$\log \frac{P_{X_2}}{P_{X_2}(0)}$$

and the deviation from stoichiometry is schematically presented in Figure 5.1.

For the composition $M_{1-x}X$ the electroneutrality condition reads

$$[e'] + [V_M'] = [h^{\bullet}] + [M_i^{\bullet}] \quad (5.26)$$

With K_F , K_a , K_i and the condition $K_i \ll K_a$, $K_i \ll K_a P_{X_2}^{\frac{1}{2}}$ ($= [V_M'] [h^{\bullet}]$) one obtains

$$[h^{\bullet}]^2 = \frac{K_a^2 P_{X_2}}{K_F + K_a P_{X_2}^{\frac{1}{2}}} \quad (5.27)$$

For small deviations from stoichiometry, i.e., $K_F \gg K_a P_{X_2}^{\frac{1}{2}}$ the concentration of the electron holes is given by

$$[h^{\bullet}] = K_a K_F^{-\frac{1}{2}} P_{X_2}^{\frac{1}{2}} \quad (5.28)$$

For large deviations from stoichiometry, i.e., $K_F \ll K_a P_{X_2}^{\frac{1}{2}}$ one obtains

$$[h^{\bullet}] = [V_M'] = K_a^{\frac{1}{2}} P_{X_2}^{\frac{1}{4}} \quad (5.29)$$

FIGURE 5.1. Schematic graph of the relative partial X_2 pressure as a function of the deviation x from the stoichiometric composition.

For the composition $M_{1+x}X$ it can be shown that for small deviations from the stoichiometry the electron concentration reads

$$[e'] = K_b K_F^{-\frac{1}{2}} P_{X_2}^{-\frac{1}{2}} (K_F \gg K_b P_{X_2}^{-\frac{1}{2}}) \quad (5.30)$$

and for large deviations

$$[e'] = [M_i'] = K_b^{\frac{1}{2}} P_{X_2}^{-\frac{1}{4}} \quad (K_F \ll K_b P_{X_2}^{-\frac{1}{2}}) \quad (5.31)$$

Thus, in general, the concentration of the defects can be represented by

$$[i] = P_{X_2}^{n_i/2} \prod_r K_r^{S_i} \quad (5.32)$$

Here, n_i and s_i are characteristic exponents (simple rational numbers). K_r is the equilibrium constant of the r -th defect reaction.

The results are commonly represented by the Kröger-Vink or Brouwer diagrams, i.e., plots of log defect concentration vs. log component activity, which quantitatively express the variation of defect chemistry within a given phase.^{10,61}

The partial pressure dependence, according to

FIGURE 5.2. Kröger-Vink diagram of the model material MX with Frenkel disorder.

$$\left(\frac{d \log [i]}{d \log P_{X_2}^{1/2}} \right)_{P,T} = n_i, \quad (5.33)$$

is represented by straight lines in the Kröger-Vink diagram, as shown in Figure 5.2.

If aliovalent impurities are present, these have to be included into Equation (5.26) because they influence the point defect concentrations. A great number of studies, including extrinsic disorder in nonstoichiometric compounds, have appeared in the literature, and the concepts have been extended to ternary and multinary compounds. Before discussing these compounds, the concepts will be applied to transition metal oxides, because these represent an important technological class of materials.

2. Transition Metal Oxides

If a transition metal oxide MO exhibits Frenkel disorder, the following gas-solid equilibria can be established, thus forming nonstoichiometric $M_{1\pm x}O$,

The equilibrium constants are, respectively,

$$K_1 = \frac{[M_i^{\bullet\bullet}][e']^2}{a_M} \quad (5.38)$$

and

$$K_2 = \frac{[e']^2}{a_M[V_M'']} \quad (5.39)$$

With Equation (5.3) one obtains

$$K_1 = K_2 K_F \quad (5.40)$$

For the anion-excess oxide, the equilibrium constants are, respectively,

$$K_3 = \frac{[h^{\bullet}]^2[V_M'']}{P_{O_2}^{\frac{1}{2}}} \quad (5.41)$$

and

$$K_4 = \frac{[h^{\bullet}]^2}{[M_i^{\bullet\bullet}]P_{O_2}^{\frac{1}{2}}} \quad (5.42)$$

Here one obtains with Equation (5.3)

$$K_3 = K_4 K_F \quad (5.43)$$

The thermal generation of intrinsic electronic disorder is given by

with

$$K_i = [e'][h^{\bullet}] \quad (5.45)$$

Here we assume the defects to be fully ionized.

For the thermodynamic treatment of the point defect equilibria, one has to take into account the electroneutrality condition

$$[e'] + 2[V_M''] = [h^{\bullet}] + 2[M_i^{\bullet\bullet}] \quad (5.46)$$

For the determination of the dependence of the point defect concentrations on the oxygen partial pressure, one again has to distinguish between the regions of small and large deviations from stoichiometry, that is, for

$$\underline{M_{1+x}O}: \quad [e'] + 2[V_M''] = 2[M_i''] \quad (5.47)$$

and

$$[e'] \approx 2[M_i''] \quad (5.48)$$

and for

$$\underline{M_{1-x}O}: \quad 2[V_M''] = [h^*] + 2[M_i''] \quad (5.49)$$

and

$$2[V_M''] \approx [h^*] \quad (5.50)$$

Electroneutrality Equations (5.47) and (5.49) hold for small deviations from stoichiometry, while Equations (5.48) and (5.50) hold for large deviations from stoichiometry.

The dependence of the point defect concentrations on the oxygen partial pressure can be derived using the expressions for K_1 – K_4 and K_i , and the reduced electroneutrality conditions (5.47) to (5.50). For the regions of small deviations from stoichiometry, one obtains for

$$\underline{M_{1+x}O}: \quad [e'] = K_i K_3^{-\frac{1}{2}} K_F^{\frac{1}{4}} P_{O_2}^{-\frac{1}{4}} \quad (5.51)$$

and for

$$\underline{M_{1-x}O}: \quad [h^*] = K_3^{\frac{1}{2}} K_F^{-\frac{1}{4}} P_{O_2}^{+\frac{1}{4}} \quad (5.52)$$

For large deviations from stoichiometry, the dependences are

$$\underline{M_{1+x}O}: \quad [e'] = (2K_F)^{\frac{1}{3}} K_3^{-\frac{1}{3}} P_{O_2}^{-\frac{1}{6}} \quad (5.53)$$

and

$$\underline{M_{1-x}O}: \quad [h^*] = \left(\frac{K_4 K_i}{2} \right)^{\frac{1}{3}} P_{O_2}^{+\frac{1}{6}} \quad (5.54)$$

In the case of large deviations from stoichiometry, simple associates or more extended defect clusters can be formed. One example is the Koch–Cohen defect cluster in nonstoichiometric wüstite (FeO). This defect cluster bears a strong resemblance to the structure of Fe_3O_4 . One can think of nonstoichiometric FeO as fragments of Fe_2O_3 intergrown in the rock salt structure of FeO.²² Another well-known cluster in the oxide-interstitial defect cluster is

anion-excess fluorite-structured UO_{2+x} . This cluster, comprising an O_i'' and two relaxed oxide ions, thus leading to $2 \text{V}_{\text{O},r}^{\bullet\bullet}$ and $2 \text{O}_{i,r}''$, in addition to the regular interstitial, has been used to explain extended defect clustering in fluorite-type anion-excess solid solutions in the systems $\text{MeF}_2\text{-ReF}_3$ and $\text{MeF}_2\text{-UF}_4$. Here, Me stands for an alkaline earth metal and Re for a rare earth metal.

The defect chemistry of nonstoichiometric transition metal oxides has been studied extensively, and many of these studies^{62,63} have been reviewed.^{15,19,54,64-68}

Schematic Kröger–Vink diagrams of metal oxides have been reported,^{15,68} and these resemble the defect diagram in Figure 5.2 as expected.

B. GENERALIZED APPROACH TO THE DEFECT CHEMISTRY OF TERNARY COMPOUNDS

For the simple binary compounds discussed in Sections II.A.1 and II.A.2, at given P and T, usually the partial pressure of the electronegative element is used. In ternary compounds a second component activity has to be determined, leading to a three-dimensional representation for the relationships between defect concentrations and component activities.

In ternary compounds of the type (A,B)X, the point defect concentrations and hence the deviation from stoichiometry depend on the concentrations of the two cations. Since in general the equilibrium constants of the different point defect equilibria in ternary compounds are composition dependent, their thermodynamic treatment is more difficult, and usually much more experimental data are required than in the case of the binary compounds. The complexity of the ternary compounds is the reason why point defect chemistry has been worked out more or less quantitatively only for some oxide and fluoride systems, using the concepts of Kröger and Vink,^{8,10} Kröger,¹⁰ Schmalzried and Wagner,²⁵ and Schmalzried.²⁶

Schmalzried²⁶ has pointed out that the theories of the defect chemistry of spinels can be generalized and be applied to all ternary compounds. Groenink³⁴ and Groenink and Binsma⁶⁹ made this generalization for ternary compounds comprising two cations and one anion, i.e., $\text{A}_a\text{B}_b\text{X}_c$ with the cations $\text{A}^{\alpha+}$ and $\text{B}^{\beta+}$, and the anion $\text{X}^{\gamma-}$. The compound is formed from the binary compounds A_pX_q and B_rX_s . They choose $\beta \geq \alpha$. In this section the generalization reported by Groenink and Binsma⁶⁹ will be summarized.

For the ternary compound the following independent variables are chosen, i.e., total pressure P, temperature T, partial pressure P_{X_2} , and the activity $a_{\text{A}_p\text{X}_q}$ of the binary compound A_pX_q , hereafter referred to as a_0 . The following defects can be present in $\text{A}_a\text{B}_b\text{X}_c$:

$$\text{A}_i^{(\alpha-j)\bullet}, \quad j = 0, 1, \dots, \alpha$$

$$\text{B}_i^{(\beta-k)\bullet}, \quad k = 0, 1, \dots, \beta$$

$$\text{X}_i^{(\gamma-l)'}, \quad l = 0, 1, \dots, \gamma$$

$$\text{V}_A^{(\alpha-j')'}, \quad j' = 0, 1, \dots, \alpha$$

$$\text{V}_B^{(\beta-k')'}, \quad k' = 0, 1, \dots, \beta$$

$$\text{V}_x^{(\gamma-l')'}, \quad l' = 0, 1, \dots, \gamma$$

$$A_B^{(\beta-\alpha-m)'}, \quad m = 0, 1, \dots, \beta - \alpha$$

$$B_A^{(\beta-\alpha-n)^*}, \quad n = 0, 1, \dots, \beta - \alpha$$

$$e'$$

$$h^*$$

Here, ionization of the defects is assumed to occur. The total electroneutrality condition is, taking into account the possible defects,

$$\begin{aligned} [e'] + \sum_{j'=0}^{\alpha-1} (\alpha - j') [V_A^{(\alpha-j')}] + \sum_{k'=0}^{\beta-1} (\beta - k') [V_B^{(\beta-k')}] + \sum_{l=0}^{\gamma-1} (\gamma - 1) [X_i^{(\gamma-1)}] \\ + \sum_{m=0}^{\beta-\alpha-1} (\beta - \alpha - m) [A_B^{(\beta-\alpha-m)'}] = [h^*] + \sum_{j=0}^{\alpha-1} (\alpha - j) [A_i^{(\alpha-j)^*}] \\ + \sum_{k=0}^{\beta-1} (\beta - k) [B_i^{(\beta-k)^*}] + \sum_{l'=0}^{\gamma-1} (\gamma - 1') [V_X^{(\gamma-l')}] \\ + \sum_{n=0}^{\beta-\alpha-1} (\beta - \alpha - n) [B_A^{(\beta-\alpha-n)^*}] \end{aligned} \quad (5.55)$$

Usually, for a given combination of thermodynamic variables, the concentrations of two defects of opposite sign are much higher than the concentrations of all other defects. Using this approximation, Equation (5.55) reduces to a form for this majority defect pair, i.e., $[V_A^{\alpha'}] = [A_i^{\alpha'}]$ for the majority defect pair $V_A^{\alpha'}$, $A_i^{\alpha'}$.

Table 5.2 presents a number of defect equilibria and equilibria with the gas phase.

1. Variation of Defect Concentrations with a_0 and P_{X_2}

If the variation of the concentration of a defect j as a result of a change in a_0 and P_{X_2} occurs between equilibrium states in a reversible way, one can write at fixed P and T ,

$$d[j] = \left(\frac{\partial [j]}{\partial P_{X_2}} \right)_{P, T, a_0} dP_{X_2} + \left(\frac{\partial [j]}{\partial a_0} \right)_{P, T, P_{X_2}} da_0 \quad (5.68)$$

It is more convenient, however, to consider the change of the logarithm of the defect concentration, because this is a simple function of α , β , γ , a , b , and p , whereas $d[j]$ still contains unknown defect concentrations. For the calculation of

$$\left(\frac{\partial \log [j]}{\partial \log P_{X_2}} \right)_{P, T, a_0} \quad \text{and} \quad \left(\frac{\partial \log [j]}{\partial \log a_0} \right)_{P, T, P_{X_2}}$$

four equilibria are required, viz., Equations (5.64) to (5.67).

TABLE 5.2
Some Internal Equilibria and Equilibria with the Gas Phase

$A_A^x + V_i^x \rightleftharpoons A_i^\alpha + V_A^{\alpha'}$	$K_{AF} = [A_i^{\alpha'}] [V_A^{\alpha'}]$	(5.56)
$X_X^x + V_i^x \rightleftharpoons X_i^{\gamma'} + V_X^{\gamma'}$	$K_{aF} = [X_i^{\gamma'}] [V_X^{\gamma'}]$	(5.57)
$B_A^{(\beta-\alpha)'} + V_i^x \rightleftharpoons B_i^{\beta'} + V_A^{\alpha'}$	$K_4 = \frac{[B_i^{\beta'}] [V_A^{\alpha'}]}{[B_A^{(\beta-\alpha)'}]}$	(5.58)
$O \rightleftharpoons aV_A^{\alpha'} + bV_B^{\beta'} + cV_X^{\gamma'}$	$K_S = [V_A^{\alpha'}]^a [V_B^{\beta'}]^b [V_X^{\gamma'}]^c$	(5.59)
$O \rightleftharpoons e' + h'$	$K_i = [e'] [h']$	(5.60)
$X_i^{\gamma'} + h' \rightleftharpoons X_i^{(\gamma-l)'}$	$K_5 = \frac{[X_i^{(\gamma-l)' }]}{[X_i^{\gamma'}] [h']^1}$	(5.61)
$A_p X_q(g) + pV_A^{\alpha'} + qV_i^x \rightleftharpoons pA_A^x + qX_i^{\gamma'}$	$K_6 = \frac{[A_A^x]^p [X_i^{\gamma'}]^q}{a_{A_p X_q} [V_A^{\alpha'}]^p}$	(5.62)
$2A_p X_q(g) + 2pV_A^{\alpha'} \rightleftharpoons 2pA_A^x + 2p\alpha e' + qX_2(g)$	$K_7 = \frac{[e']^{2p\alpha} \cdot P_{X_2}^q}{a_{A_p X_q}^2 [V_A^{\alpha'}]^{2p}}$	(5.63)
$A_p X_q(g) + pV_A^{\alpha'} + qV_X^{\gamma'} \rightleftharpoons pA_A^x + qX_X^x$	$K_8 = a_{A_p X_q} [V_A^{\alpha'}]^p [V_X^{\gamma'}]^q$	(5.64)
$B_r X_s(g) + rV_B^{\beta'} + sV_X^{\gamma'} \rightleftharpoons rB_B^x + sX_X^x$	$K_9 = a_{B_r X_s} [V_B^{\beta'}]^r [V_X^{\gamma'}]^s$	(5.65)
$raA_p X_q(g) + pbB_r X_s(g) \rightleftharpoons prA_a B_b X_c$	$K_{10} = a_{A_p X_q}^{ra} \cdot a_{B_r X_s}^{pb}$	(5.66)
$2X_X^x \rightleftharpoons 2V_X^{\gamma'} + 2\gamma e' + X_2(g)$	$K_{11} = [V_X^{\gamma'}]^2 [e']^{2\gamma} P_{X_2}$	(5.67)

Defining

$$\left(\frac{\partial \log [V_A^{\alpha'}]}{\partial \log a_0} \right)_{P, T, P_{X_2}} = \xi_1,$$

$$\left(\frac{\partial \log [V_B^{\beta'}]}{\partial \log a_0} \right)_{P, T, P_{X_2}} = \xi_2,$$

$$\left(\frac{\partial \log[V_X^{\gamma\cdot}]}{\partial \log a_0} \right)_{P,T,P_{X_2}} = \xi_3,$$

and

$$\left(\frac{\partial \log[e']}{\partial \log a_0} \right)_{P,T,P_{X_2}} = \xi_4,$$

and differentiating the logarithm of Equations (5.64) to (5.67) with respect to $\log a_0$, one obtains

$$p\xi_1 + q\xi_3 = -1 \quad (5.69)$$

$$r\xi_2 + s\xi_3 = \frac{ar}{bp} \quad (5.70)$$

$$\xi_3 + \gamma\xi_4 = 0 \quad (5.71)$$

A fourth relation between ξ_1 , ξ_2 , ξ_3 , and ξ_4 can be found by differentiating the logarithm of the electroneutrality condition for the majority defect pair considered with respect to $\log a_0$. This electroneutrality condition can then be rewritten in the form:

$$x_1\xi_1 + x_2\xi_2 + x_3\xi_3 + x_4\xi_4 = 0 \quad (5.72)$$

with the aid of the following relation,

$$\frac{\partial \log[j]}{\partial \log x} = a_1 \frac{\partial \log[V_A^{\alpha\cdot}]}{\partial \log x} + a_2 \frac{\partial \log[V_B^{\beta\cdot}]}{\partial \log x} + a_3 \frac{\partial \log[V_X^{\gamma\cdot}]}{\partial \log x} + a_4 \frac{\partial \log[e']}{\partial \log x} \quad (5.73)$$

in which x denotes either a_0 or P_{X_2} .

The numbers x_1 , x_2 , x_3 , and x_4 in Equation (5.72) are characteristic for the given majority defect pair. Solving the four linear equations in ξ_i yields the values presented in Table 5.3.

The values for a_1 , a_2 , a_3 , and a_4 are given in Table 5.4.

2. Composition and Defect Chemistry

The compound $A_aB_bX_c$ is made up of $L \cdot A_pX_q + M \cdot B_rX_s + NX_2$. L , M , and N are integers, L and M strictly positive, and N positive, zero, or negative. The total concentrations of A , B , and X are

$$[A]_{\text{tot}} = L \cdot p \quad (5.74)$$

$$[B]_{\text{tot}} = M \cdot r \quad (5.75)$$

$$[X]_{\text{tot}} = L \cdot q + M \cdot s + 2N \quad (5.76)$$

TABLE 5.3
The Dependence of the Logarithm of Some Defects on the Logarithm of a_0 and P_{X_2}

[j]	$\left(\frac{\partial \log [j]}{\partial \log a_0}\right)_{P, T, p_{x_2}}$	$\left(\frac{\partial \log [j]}{\partial \log P_{x_2}}\right)_{P, T, a_0}$
$V_A^{\alpha'}$	$\frac{-(a \alpha + \beta b) x_2 - b(-\gamma x_3 + x_4)}{C}$	$\frac{\alpha x_4}{B}$
$V_B^{\beta'}$	$\frac{(\alpha a + \beta b) x_2 + a(-\gamma x_3 + x_4)}{C}$	$\frac{\beta x_4}{B}$
$V_X^{\gamma'}$	$\frac{-b \gamma x_1 + a \gamma x_2}{C}$	$\frac{-\gamma x_4}{B}$
e'	$\frac{b x_1 - a x_2}{C}$	$\frac{-a x_1 - \beta x_2 + \gamma x_3}{B}$
$C = p b\left(\alpha x_1 + \beta x_2 - \gamma x_3 + x_4\right)$		$B = 2 \gamma\left(\alpha x_1 + \beta x_2 - \gamma x_3 + x_4\right)$

The composition of the compound is known if the ratios

$$\frac{[A]_{tot}}{[B]_{tot}} \text{ and } \frac{[X]_{tot}}{[A]_{tot}}$$

are known. For the ideal compound composition these ratios read

$$\frac{[A]_{tot}}{[B]_{tot}} = \frac{L \cdot p}{M \cdot r} = \frac{a}{b} \quad (5.77)$$

and

$$\frac{[X]_{tot}}{[A]_{tot}} = \frac{L \cdot p + M \cdot s + 2N}{L \cdot p} = \frac{c}{a} \quad (5.78)$$

The deviation from the ideal composition can be described by two parameters, i.e., Δx , the deviation from molecularity, and Δy , the deviation from stoichiometry. An excess $A_p X_q$ gives $\Delta x > 0$, and an excess $B_r X_s$ $\Delta x < 0$. Δy is the parameter which determines, at a fixed ratio $\frac{L}{M}$, whether there is an excess X_2 ($\Delta y > 0$) or a deficiency X_2 ($\Delta y < 0$). The compound has the ideal composition for $\Delta x = \Delta y = 0$. Defined in terms of Equations (5.77) and (5.78), these parameters are

TABLE 5.4
Coefficients a_1, a_2, a_3 , and a_4 in Equation 5.73
for All Defects Considered

[j]	a_1	a_2	a_3	a_4
$A_i^{(\alpha-j)^*}$	-1	0	0	+j
$B_i^{(\beta-k)^*}$	0	-1	0	+k
$X_i^{(\gamma-l)^*}$	0	0	-1	+l
$V_A^{(\alpha-j')^*}$	+1	0	0	-j'
$V_B^{(\beta-k')^*}$	0	+1	0	-k'
$V_x^{(\gamma-l')^*}$	0	0	+1	-l'
$A_B^{(\beta-\alpha-m)^*}$	-1	+1	0	-m
$B_A^{(\beta-\alpha-n)^*}$	+1	-1	0	+n
e^*	0	0	0	1
h^*	0	0	0	-1

$$\Delta x = \frac{r}{p} \left[\frac{[A]_{tot}}{[B]_{tot}} - \frac{a}{b} \right] \quad (5.79)$$

and

$$\Delta y = \frac{\gamma[X]_{tot}}{\alpha[A]_{tot} + \beta[B]_{tot}} - 1 \quad (5.80)$$

Groenink³⁴ has demonstrated that a given majority defect pair can only exist in a compound if certain conditions with regard to Δx and Δy are fulfilled. The conditions are specific for the majority defect pair. For Δx and Δy , general relations including all the possible point defects were derived,³⁴ and the condition for a given majority defect pair are then found by neglecting all the other point defect concentrations in the general relations for Δx and Δy . A complete survey of the conditions for all the possible majority defect pairs has been reported by Groenink³⁴ and Groenink and Binsma.⁶⁹ For given values of Δx and Δy , only a limited number of majority defect pairs can exist in a compound, and which of these pairs occurs in practice depends upon temperature, pressure, and formation energy of the various defects.

FIGURE 5.3. Kröger-Vink diagram of the model material $A^{2+}B^{6+}O_4^{2-}$, exhibiting deviations from molecularity.

3. Defect Diagrams

The Kröger-Vink diagrams can be constructed using Tables 5.3 and 5.4. It is evident that a_0 and P_{X_2} may vary only within the range of homogeneity of $A_aB_bX_x$. Figure 5.3 is the Kröger-Vink diagram of a model material ABO_4 , in which A, B, and O are ions with a charge +2, +6, and -2, respectively. In this diagram Δx varies and $\Delta y = 0$. For variations in Δy at fixed a_{AO} , the diagram closely resembles that in Figure 5.2.

The Kröger-Vink diagrams of compounds ABX_4 , in which A, B, and X are ions with charge +1, +3, and -1 are presented in Figures 5.4 and 5.5. It is assumed that the model material exhibits anti-Frenkel disorder.

Figure 5.4 presents the relations between the point defect concentrations and a deviation from stoichiometry, while in Figure 5.5 these relations are plotted in the case of deviations from the stoichiometry.²⁷

The quantitative relations between the point defect concentrations and the compound activities are very useful in interpreting electrical properties of solid electrolytes and MIECs. The point defect-composition relations also define the electrolytic domain of a solid electrolyte, and hence determine experimental conditions to be fulfilled in order for the materials to be applicable in solid state electrochemical devices.

FIGURE 5.4. Kröger-Vink diagram of the model material $A^+ B^{3+} X_4^-$, exhibiting deviations from molecularity.

FIGURE 5.5. Kröger-Vink diagram of the model material $A^+ B^{3+} X_4^-$, exhibiting deviations from stoichiometry for $\Delta x > 0$.

It should be borne in mind, though, that the traditional mass action laws which govern the point defect concentrations are based on the assumptions of negligible interactions and random distributions. They are not applicable in high-defect concentration regimes. A general defect chemistry formulation based on statistical thermodynamic consideration has recently been developed by Ling.⁷⁰ His statistical thermodynamic formulation explicitly incorporates long-range Coulombic interactions and the generalized exclusion effects. For solid solutions in the system $\text{CeO}_2\text{--CaO}$, Ling found good agreement between calculated and experimental conductivity data. The reaction enthalpies are found to be strongly influenced by defect interactions. Only at very high defect concentrations do the effects of defect exclusions become significant.

4. Application to Several Ternary Compounds

While intrinsic disorder of the Schottky, Frenkel, or anti-Frenkel type frequently occurs in binary metal oxides and metal halides, i.e., Equations (5.1), (5.3), and (5.5), Schottky disorder is seldomly encountered in ternary compounds. However, in several studies Schottky disorder has been proposed to occur in perovskite oxides. Cation and anion vacancies or interstitials can occur in ternary compounds, but such defect structures are usually to be related with deviations from molecularity (viz. Sections II.B.2 and II.B.3), which in fact represent extrinsic disorder and not intrinsic Schottky disorder. From Figures 5.3 and 5.4 it is apparent that deviations from molecularity always influence ionic point defect concentrations, while deviations from stoichiometry always lead to combinations of ionic and electronic point defects, as can be seen from Figures 5.2 and 5.5.

A material which has attracted widespread attention is the perovskite oxide LaCrO_3 , and especially the LaCrO_3 -based solid solutions. It is the state-of-the-art interconnection material in the solid oxide fuel cell (SOFC). LaCrO_3 is known to be a p-type conductor, owing to the presence of electron holes in the 3d-band of the Cr ions, i.e., $\text{Cr}_{\text{Cr}}^\bullet$. Conduction occurs by the thermally activated hopping of localized charge carriers ($\text{Cr}_{\text{Cr}}^\bullet$).⁷¹ Doping with relatively small amounts of Mg^{2+} , Sr^{2+} , or Ca^{2+} enhances the electronic conductivity. Under oxidizing conditions, charge compensation takes place by a Cr^{3+} to Cr^{4+} transition, thereby increasing the electronic charge carrier density. Under reducing conditions, charge compensation takes place under the formation of oxygen ion vacancies, and no increased electronic conductivity is expected. The interconnection material in an SOFC operates under these extreme conditions. For Mg^{2+} -doped LaCrO_3 the defect Mg_{Cr}' is formed. The acceptor is electrically compensated by the Cr^{3+} to Cr^{4+} transition^{71,72} or by $\text{V}_{\text{O}}^{\bullet\bullet}$. The electroneutrality condition reads

$$[\text{Mg}_{\text{Cr}}'] = [\text{Cr}_{\text{Cr}}^\bullet] + 2[\text{V}_{\text{O}}^{\bullet\bullet}] \quad (5.81)$$

Here, anti-Frenkel disorder is assumed to occur. The corresponding defect equilibrium can be written as

For this material other defect models have been proposed.⁷³⁻⁷⁶

Flandemeyer et al.⁷³⁻⁷⁴ and Anderson et al.⁷⁵ used a defect model based on Schottky disorder, i.e.,

To determine the influence of the oxygen partial pressure on the oxygen ion vacancy concentration, the following defect equilibrium was assumed:

However, it is unlikely that this defect equilibrium determines the oxygen ion vacancy concentration in Mg-doped $LaCrO_3$, as the presence of trivalent cation vacancies in ternary metal oxides is not favored thermodynamically.¹⁰

In the proposed defect models it is assumed that all defects are distributed randomly over the lattice. Singhal et al.,⁷⁶ Van Roosmalen and Cordfunke,⁷⁷ and Van Roosmalen⁷⁸ have proposed defect structures including defect clusters comprising $V_O^{\bullet\bullet}$ next to regular Cr_{Cr}^x ions, and $(Mg_{Cr}' - V_O^{\bullet\bullet} - Mg_{Cr}')^x$ clusters. While no rationale was presented for the trapping of oxygen ion vacancies at regular Cr_{Cr}^x sites, the $(2Mg_{Cr}' \cdot V_O^{\bullet\bullet})^x$ cluster model seems to describe the experimentally determined oxygen ion vacancy concentrations as a function of P_{O_2} by Flandemeyer et al.^{73,74} and Anderson et al.⁷⁵ The corresponding defect equilibrium including these clusters can be represented by

Usually, the interconnection material Mg-doped $LaCrO_3$ is produced using electrochemical vapor deposition (EVD). EVD is the key technology developed by Westinghouse for the production of gas tight layers of SOFC solid electrolyte and interconnection materials on porous electrode structures. Recently, Van Dieten et al.⁷⁹⁻⁸¹ used anti-Frenkel disorder in $LaCrO_3$ along with Equations (5.81) and (5.82) to quantitatively model the EVD growth of Mg-doped $LaCrO_3$.⁸¹

The clustering concept was not employed in the modeling of the EVD growth, because the EVD process is carried out at temperatures in the range of 1400 to 1600 K. At these temperatures these defect clusters are assumed to be not stable.

The presented concepts for Δx and Δy have been used in other studies on SOFC electrode and interconnection materials exhibiting mixed ionic (via $V_O^{\bullet\bullet}$) and electronic conductivity.⁸²⁻⁸⁴

The perovskites $La_{1-x}M_xB_{O_{3-\delta}}$ ($M = Sr, B = Co, Cr, Fe, Mn$) have been reviewed by Alcock et al.⁸⁵ in terms of their stability in temperature and oxygen partial pressure of operation as active sensor material, nonstoichiometry, conductivity, and catalytic properties, and the effect of the strontium content, x .

The deviations from stoichiometry in these perovskites are accounted for using Equation (5.67). The defect models used for the MIECs discussed so far are all concordant with the defect model used by Van Dieten et al.⁷⁹⁻⁸¹ for the modeling of the EVD growth of the SOFC interconnection material.

Another important class of ternary oxides with mixed ionic-electronic conductivity is based on the pyrochlore system, $A_2B_2O_7$. Especially, Tuller and co-workers⁸⁶⁻⁸⁹ have studied the defect chemistry of nominally pure, and donor- and acceptor-doped $Gd_2Ti_2O_7$ (GT). They have demonstrated that mixed ionic and electronic conductivity can be controlled over wide limits in the pyrochlore oxides described by compositions $Gd_2(Ti_{1-x}Zr_x)_2O_7$ (GZT) and $Y_2(Ti_{1-x}Zr_x)_2O_7$ (YZT) by control of both the parameter x and by doping. If GT is doped with Ca ⁸⁶ or by selecting $x > 0.4$ in GZT,^{87,88} an excellent solid electrolyte is obtained. Reduced or donor-doped GT exhibits predominantly a P_{O_2} -dependent semiconducting behavior.⁹⁰

The ionic conductivity increases in GZT as Zr substitutes for Ti due to increasing anion disorder, and this appears to be related to the decrease in the average B to A cation radius ratio, which, in the limit, leads to full disordering to the defect fluorite structure $(A,B)_4O_7$. Also, the doping with multivalent donors and acceptors has been studied. An in-depth review has been reported by Spears and Tuller,⁹¹ in which the application of defect modeling of the pyrochlores to materials design is discussed.

The electrical properties of the titanate-based pyrochlores can be described by point defect models in which the acceptor (A) and donor (D) impurities are compensated by oxide ion vacancies, or oxide ion interstitials, respectively.⁹² The principal defect reactions include the redox reaction, Equation (5.67), the Frenkel disorder, Equation (5.57), dopant ionization, intrinsic electronic disorder, Equation (5.60), and the electroneutrality relation. For these compounds the total electroneutrality condition given by Equation (5.55) is, on the one hand, reduced, taking Equation (5.57) into account, and is, on the other hand, extended to include acceptor and donor impurities. In addition, defect association is included explicitly.

The electroneutrality relation thus reads,

$$2[O_i''] + [O_i'] + [e'] + [A'] + [(D \cdot O_i)'] = 2[V_o''] + [V_o'] + [h'] + [D'] + [(A \cdot V_o)'] \quad (5.86)$$

Now the more complex defect equilibria are treated with the aid of numerical methods. Spears and Tuller⁹¹ show how this approach can be used, not only to extract principal defect thermodynamic and kinetic data, but also to assist in the design and optimization of materials. Using all possible defect reactions and defect equilibria, combined with Equation (5.86), one arrives at an eight-order polynomial in, for instance, $[e']$, which can only be solved numerically. In a simplified approach for the nominally pure material, expressions for $[e']$ and $[h']$ are obtained, which are concordant to Equations (5.51) and (5.52). The simple Kröger–Vink diagram for such a defect situation has already been presented by Kofstad.⁹³

For the more complex extrinsic defect structure, the Newton–Raphson method was used to numerically solve the high-order polynomials, which come about during attempts to solve the simultaneous defect equations, using the complete electroneutrality condition. For acceptor-doped $Gd_2Ti_2O_7$ with strong acceptor-oxide ion vacancy association, Spears and Tuller⁹¹ report the Kröger–Vink diagram for the $\log P_{O_2}$ (atm) regime -50 to $+50$. Using this approach, mixed conduction in $Gd_2(Zr_{0.3}Ti_{0.7})_2O_7$ was modeled in terms of the P_{O_2} dependence of the point defect concentrations $[V_o'']$, $[O_i']$, and $[e']$ for $\log P_{O_2}$ (atm) in the region -25 to $+5$. For $\log P_{O_2} < -15$ the reduced electroneutrality condition

$$2[V_o''] = [e'] \quad (5.87)$$

holds, while for larger P_{O_2} values the condition reads,

$$2[V_o''] = [e'] + 2[O_i''] \quad (5.88)$$

In GZT, with $x = 0.3$, and doped with an acceptor of 1% substitution for Gd, i.e., A'_{Gd} , the oxide ion vacancy concentration is increased at the expense of $[O_i'']$, viz. Equation (5.57). Likewise, the electron hole conductivity is increased at the expense of the electron conduction.

The calculated P_{O_2} dependencies at 1373 K of the predominant defect concentrations in $Gd_2(Zr_{0.3}Ti_{0.7})_2O_7$ reveal that a transition from ionic disorder, $[V_o''] = [O_i'']$, at high P_{O_2} to

reduction control $[e'] = 2 [V_O^{\bullet\bullet}]$ occurs at $P_{O_2} \approx 10^{-15}$ atm. For $P_{O_2} \approx 10$ atm a p-n junction occurs.⁹¹ GZT doped with 1 at. percent acceptor, A'_{Gd} , reveals a narrowing of the defect regime defined by $[e'] = 2 [V_O^{\bullet\bullet}]$.

Also, in acceptor-doped perovskites $(Ba_xSr_{1-x})TiO_3$ the principal defects and their dependence on P_{O_2} , dopant concentrations, and temperature could be obtained.^{91,94} The approach has recently also been applied successfully to the pyrochlore system $(Gd_{1-x}Ca_x)_2Sn_2O_{7\pm\delta}$.⁹⁵

For cost and stability reasons, many materials studies for SOFCs are directed toward lowering the operating temperature from 1000°C to below 800°C. Since the pioneering work of Iwahara and co-workers,^{96,97} who discovered high-temperature proton conductivity in the perovskite oxides $SrCeO_3$ and $BaCeO_3$, cerate-based perovskite-type oxide ceramics have attracted widespread attention. Doping with trivalent cations, which substitute for cerium, is essential for the occurrence of proton conduction in hydrogen-containing ambients at high temperatures.

$SrCe_{0.95}Y_{0.05}O_{3-\alpha}$, $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$, and $BaCe_{0.9}Nd_{0.1}O_{3-\alpha}$ are examples of this class of proton-conducting oxide ceramics. The state of the art has been reviewed by Iwahara.^{98,99} Besides application in SOFCs, these solid electrolytes have been explored for use in high-temperature steam electrolyzers, hydrogen sensors and pumps, and electroceramic reactors for (de-)hydrogenation processes.⁹⁸⁻¹⁰⁵ A major disadvantage of this class of materials is their instability in CO_2 -containing atmospheres.^{106,107}

The defect chemistry of these oxides has been studied in relation to the formation of protons in equilibrium with different ambients. The general formula for these oxides can be represented by

$$(M_M^x) (Ce_{Ce}^x)_{1-x} (Me'_{Ce})_x (O_O^x)_{3-\frac{1}{2}x} (V_O^{\bullet\bullet})_{\frac{x}{2}} \quad (5.89)$$

with electroneutrality condition.

$$[Me'_{Ce}]_x = 2[V_O^{\bullet\bullet}]$$

Here, M represents Sr, or Ba, and Me a rare earth element. Usually x is smaller than 0.1.

In dry oxygen atmosphere the formation of electron holes is described by

In a wet oxygen atmosphere both protons and electron holes are generated according to

and

The equilibrium state of the oxides can be described by any two of these equilibrium reactions, as

$$K_{H,1} = K_h K_{H,2} \quad (5.93)$$

In a dry hydrogen-containing atmosphere the equilibrium

is established.

Hence the electrical properties of the M CeO_3 -based perovskite-type oxides are quite dependent on the ambients, and can be summarized as follows:^{98,99}

- $\text{M Ce}_{1-x}\text{Me}_x\text{O}_{3-1/2x}$ exhibits electron hole conductivity, when sintered in air, and measured in a dry, hydrogen-free atmosphere.
- In atmospheres containing water vapor or hydrogen, protonic conduction increases at the expense of electronic conductivity.
- In pure hydrogen the transference number of the protons becomes unity at high temperatures.
- Mixed oxide and proton conduction occurs in the BaCeO_3 -based solid electrolytes, when utilized in a SOFC above 800°C.

The proton defect that appears in the gas–solid Equilibria (5.91), (5.92), and (5.94) is represented by H_i' . It is generally accepted that the protons are bonded to the oxide ions at regular lattice sites, thus forming a hydroxide ion, OH_O' , which is often referred to as H_i' .

Equilibrium (5.94) can also be represented by

Likewise, equilibria (5.91) and (5.92) can be rewritten to express the formation of OH_O' defects.

The introduction of protonic defects in oxides in hydrogen-containing ambients has been reported frequently, and has recently been reviewed by Colomban and Novak¹⁰⁸ and Strelkov et al.¹⁰⁸

For a doped oxide M_2O_3 exhibiting anti-Frenkel disorder, Colomban and Novak¹⁰⁸ present a schematic Kröger–Vink diagram of the extrinsic and intrinsic point defects as a function of the partial water pressure. With regard to electrical properties, the proton conductivity in the binary metal oxides is usually much lower than in the perovskite-type oxides.¹⁰⁸

C. MULTINARY COMPOUNDS

While in many of the fundamental studies of extrinsic and intrinsic disorder simple binary and ternary compounds have been investigated, the search for new materials for application in solid state batteries, high-temperature fuel cells and steam electrolyzers, electrocatalytic reactors, gas-separation membranes, smart windows, and chemical gas sensors has provided the solid state community with a wide variety of multinary materials. Prime examples are the β - and β'' -aluminas, sodium ion conductors with the NASICON framework structure, lithium ion conductors with the LISICON structures, oxide Brownmillerite systems, MIECs in the doped ABO_3 - $\text{ABO}_{2.5}$ series, layered perovskite structures, proton-conducting hydrated oxides, and the ceramic high T_c superconductors. In addition, solid solutions based on transition metal oxides represent interesting multinary compounds for solid state lithium batteries.

Many studies on multinary compounds have been reported and reviewed in the past decade.¹⁰⁹⁻¹¹⁸ Excellent surveys of crystalline multinary solid electrolytes have been reported by West¹¹⁹ and Goodenough.¹²⁰

These authors have reviewed positional disorder in stoichiometric compounds in relation to crystal structure, materials exhibiting first-order phase transformations, and diffuse, so-called Faraday, transitions, extrinsic disorder, doping strategies, and solid solutions.

In addition to these surveys, the crystal chemistry and electrochemical properties of a wide variety of multinary oxide solid electrolytes and MIECs are described in the studies reported in Reference 90. While defect chemistry has been successfully employed to model point defect generation and conduction mechanisms in nominally pure and doped binary and ternary compounds, complex defect equilibria occur in concentrated solid solutions based on ternary compounds and in multinary compounds. Usually, these complex defect equilibria are treated with the aid of numerical methods. Examples are the pyrochlores GT, GZT, and YZT as discussed in Section II.B.4.

Since the discovery of the high T_c ceramic superconductors,¹²¹ various properties of these oxide ceramics have been studied, and this is especially true for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

The critical temperature of the high T_c ceramic superconductors is intimately connected to the electronic charge carrier concentration, but at temperatures beyond the critical temperature in the nonsuperconducting state, mixed ionic–electronic conduction prevails, especially at the operation temperatures of the solid state electrochemical devices mentioned in the previous sections. In this regime a number of properties are determined by deviations from stoichiometry, which can be related to the high diffusivity of oxide ions in the structure of the high T_c ceramic superconductors. In particular, mixed ionic–electronic conductivity in $(\text{La,Sr})_2\text{CuO}_{4-x}$, $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{Bi}_2\text{Sr}_2\text{Cu}_6\text{O}_{6+x}$, and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ has attracted much attention, and has initiated defect chemical studies.^{114,115,118,122-126}

For $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ it has been established that a transition from electron hole to electron conduction occurs for $7-x < 6.3$. For $x < 0.7$ oxygen is incorporated according to

The oxide interstitials can trap an electron hole to form O_i' defects.

Here, O_i' means $(O_i'' \cdot h^*)'$ or $(O_i'' \text{Cu}_{\text{Cu}})'$. For $x < 0.7$ the isothermal conductivity reveals a $P_{\text{O}_2}^{1/2}$ dependence, indeed indicating the presence of O_i' defects.^{122,123} The actual incorporation equilibrium reaction is therefore

The preference of O_i' may be related to the fact that in the Cu plane of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, a Cu ion belongs to one structurally vacant oxygen site ($x = 1$). The incorporation of further oxygen should mainly lead to the formation of O_i^x ,

In a different approach, the deviation from stoichiometry of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ($0 \leq x \leq 0.7$) can be described using oxide ion vacancies. The gas–solid equilibrium is then described by

For nominally pure La_2CuO_4 the electron hole conductivity has been found to follow a $1/6$ power law dependence on oxygen partial pressure, indicating the gas–solid equilibrium 5.96 to occur. For Sr-doped La_2CuO_4 incorporation reactions have been presented by Opila et al.¹²⁶ to account for an increase in $[\text{h}^*]$ and $[\text{V}_\text{O}^{\bullet\bullet}]$. The total electroneutrality condition reads

$$2[\text{O}_i''] + [\text{Sr}'_{\text{La}}] + [\text{e}'] = 2[\text{V}_\text{O}^{\bullet\bullet}] + [\text{h}^*] \quad (5.101)$$

The Kröger–Vink diagrams have been calculated for $(\text{La},\text{Sr})_2\text{CuO}_4$,^{124–126} assuming fixed doping concentration and temperature. With increasing oxygen partial pressure, the following reduced electroneutrality conditions hold:

$$[\text{Sr}'_{\text{La}}] = 2[\text{V}_\text{O}^{\bullet\bullet}], [\text{Sr}'_{\text{La}}] = [\text{h}^*], \text{ and } [\text{h}^*] = [\text{O}_i'] \quad (5.102)$$

At fixed oxygen partial pressure and temperature, an increase in dopant concentration reveals the following majority defect conditions:

$$[\text{h}^*] = 2[\text{O}_i''], [\text{Sr}'_{\text{La}}] = [\text{h}^*], [\text{Sr}'_{\text{La}}] = 2[\text{V}_\text{O}^{\bullet\bullet}] \quad (5.103)$$

For $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ tentative Kröger–Vink diagrams have been constructed under the assumption of excess Y, and in the case of anti-Frenkel disorder.^{124–126} In the first case the electroneutrality conditions are with increasing P_{O_2} :

$$[\text{Y}'_{\text{Ba}}] = [\text{O}_i'], [\text{O}_i'] = [\text{h}^*] \quad (5.104)$$

In the case of Frenkel disorder the majority defect pairs are

$$[\text{O}_i'] = [\text{V}_\text{O}^{\bullet}], [\text{O}_i'] = [\text{h}^*] \quad (5.105)$$

In the high P_{O_2} regimes, i.e., $[\text{O}_i'] = [\text{h}^*]$ the concentration of $\text{O}_i^{\times}$ exceeds that of the charged point defects.

In order to obtain quantitative information on the oxide ion conductivity of high T_c ceramic superconductors, solid state electrochemical cells of the type

were studied by impedance spectroscopy.^{127,128} Here, YSZ represents yttria-stabilized zirconia. Similar cell configurations were used to study other high T_c ceramic superconductors.^{124,129}

A detailed discussion of oxide ion conductivity as obtained using the solid state electrochemical techniques is beyond the scope of this chapter.

Recent high-temperature applications of these ceramic superconductors are

- a novel chromatography detector¹³⁰
- heterogeneous catalysis,^{131–133} and
- Taguchi-type gas sensors.^{134–137}

McNamara et al.¹³⁰ used $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ as a catalyst for redox reactions between organic molecules and NO_2 in a chromatography detector, based on chemoluminescence. NO_2 is

converted to NO, which is subsequently detected via a chemoluminescence reaction with ozone, i.e.,

Hansen et al.¹³¹ have studied the oxydation of hydrocarbons to CO₂ over YBa₂Cu₃O_{7-x} as a catalyst. Besides full oxydation to CO₂, process conditions can be manipulated such as to partially oxidize hydrocarbons to a variety of industrial chemicals.

In addition to deviations from stoichiometry in the anion sublattice, YBa₂Cu₃O_{7-x} has been shown to absorb nitrogen, argon, hydrogen, and nitrogen oxide. The solubility of these gases is dependent on the oxide stoichiometry, but does not affect the perovskite structure. At 300°C, 3 mol% of NO can be dissolved into YBa₂Cu₃O_{7-x}. Desorption occurs at 500°C. The amount of absorbed NO increases with the parameter x. The NO molecules occupy the empty oxide ion sites. For high concentrations of NO, decomposition occurs according to

For simplicity, x has been assumed to be zero here.

Besides absorption of NO, YBa₂Cu₃O_{7-x} has been shown to be very effective in the catalytic decomposition of NO to N₂ and O₂. This decomposition is related to the amount of absorbed NO, and hence to the deviation from stoichiometry. This is, in fact, one of the first examples of the direct decomposition of NO in N₂ and O₂.¹³³

The high T_c ceramic superconductors have been tested in Taguchi-type gas sensors.¹³⁴⁻¹³⁷ The Taguchi gas sensor¹³⁸ is based on a semiconducting metal oxide, which exhibits a resistance change when gas molecules adsorb at the surface and influence the charge carrier concentration in the metal oxide. SnO₂, In₂O₃, and solid solutions based on these oxides have frequently been studied as active material of the Taguchi sensor.

The sensitivity to NO_x and CO_x has been investigated for YBa₂Cu₃O_{7-x}, Ba_{1.5}La_{1.5}Cu₃O_x, La_{1.85}Sr_{0.15}CuO_x, Nd_{1.85}Ce_{0.15}CuO_{4-x}, Bi₂Sr₂CuO_{6+x}, Bi₂Sr₂CaCu₂O_{8+x}, and Bi_{1.8}Pb_{0.2}Sr₂Ca₂Cu₃O_{10+x}. As expected, YBa₂Cu₃O_{7-x} reacts with NO and decomposes. Ba_{1.5}La_{1.5}Cu₃O_x and La_{1.85}Sr_{0.15}CuO_x did not show any sensitivity or selectivity of practical interest, while Nd_{1.85}Ce_{0.15}CuO_{4+x} has no selectivity for NO against CO. However, the Bi-family materials are good candidates for the development of Taguchi-type NO_x gas sensors. Bi₂Sr₂CuO_{6+x}, Bi₂Sr₂CaCu₂O_{8+x}, and Bi_{1.8}Pb_{0.2}Sr₂Ca₂Cu₃O_{10+x} exhibit good stability, reproducibility, and high selectivity against CO and CO₂. Bi₂Sr₂CaCu₂O_{8+x} exhibits the best response behavior. Composites of Bi₂Sr₂CaCu₂O_{8+x} with NiO or Fe₂O₃ show improved selectivity to NO against CO. The addition of Al₂O₃ does not affect the selectivity, but does enhance the response rate. Lithium intercalation also improved the selectivity to NO against CO. The detection mechanisms have been reported by Huang et al.,¹³⁴⁻¹³⁷ and they are based on reactions (5.96) and (5.100).

D. MULTICOMPONENT MATERIALS

Since the initial observations that the dispersion of small particles of nonconducting alumina in lithium iodide leads to a dramatic increase of the lithium ion conductivity,^{139,140} a number of studies have been devoted to the electrical properties of these multicomponent systems.¹⁴¹⁻¹⁴⁷

In general, it is found that the increase in isothermal ionic conductivity is greater the smaller the size of the dispersed inert particle, and that the conductivity-composition curve exhibits a maximum between 10 and 40 mol% of inert particles. It is generally accepted that

the conductivity enhancement can be ascribed to an increase in the defect concentration responsible for extrinsic conduction in a narrow space charge layer in the conducting compound at the grain boundary interface. This "composite effect" occurs mainly at low temperatures.¹⁴⁸ Surprisingly, practically all the studies on this composite effect have dealt with cation conducting compounds. A few studies have been reported on YSZ-alumina composites,¹⁴⁹⁻¹⁵¹ but the results have not led to firm conclusions. In a more systematic study, Filal et al.¹⁵² have investigated single crystalline, polycrystalline, and composites of YSZ. For composites comprising YSZ (9.9 mol%) and Mg-doped α -alumina of submicron size, a maximum is observed for 2 mol% α -Al₂O₃. At 250°C the grain boundary conductivity is increased by a factor of 3.7 and at 600°C by a factor of 2. While the composite effect has been established for stabilized zirconia, a mechanism is lacking. For CaF₂-Al₂O₃ composites the composite effect has been observed by Fujitsu et al.¹⁵³ Here, a complication may occur, as the ionic radii of oxide and fluoride ions are comparable, and CaF₂ exhibits anti-Frenkel disorder. As a consequence, CaF₂, or more general the alkali earth fluorides, are easily contaminated with oxide ions to form the defects $O_F' + V_F'$. If at the interface CaF₂-Al₂O₃ this doping effect occurs, it may mask space charge effects.

Maier^{154,155} has calculated the concentration profiles of minority charge carriers in ideal space charge regions. In addition, the solid state electrochemical Hebb-Wagner polarization technique was extended to the case of multicomponent materials.¹⁵⁴ The behavior of the minority carriers in the space charge regions is determined by the profiles of the majority carriers. By applying the theoretical model on the composite AgCl- γ -Al₂O₃, Maier¹⁵⁵ found that both the electron and the electron hole conductivity increased, compared to single-phase AgCl. In contrast, a shift in charge carrier type is observed on going from pure LiI (electron holes)¹³⁹ to LiI-Al₂O₃ (electrons).¹⁴⁵ Similar observations were reported for β -AgI-alumina composites. Pure β -AgI exhibits electron conduction,¹⁴⁶ while the composite has electron hole conduction. As has been pointed out by Maier,¹⁵⁴ the extra space charge contribution due to the minority charge carriers depends sensitively on impurity levels, and these are not specified in the studies on LiI- and β -AgI-based composites.

In order to shed more light on these phenomena, Maier¹⁵⁶ has calculated the defect concentrations for ionic and electronic defects in space charge regions as a function of temperature and component activities.

Using the model compound, of which the bulk defect chemistry is treated in Section II.A.1 of this chapter, Maier constructed a Kröger-Vink diagram of the model compound MX for bulk and boundary layer. His results are schematically included in Figure 5.2, and presented in Figure 5.6.

In this example it has been assumed that the bulk structure extends up to the top surface (interface) layer, in which the excess charges are accommodated and in which the potentials and defect concentrations have discretely different values. For the top layer a linear geometry is assumed. Reaction (5.12) holds for the top layer. As long as one or both ionic point defects determine the charge density alone, both ionic point defect concentrations can be handled as a constant (cf. Reaction (5.15)), as is done for the bulk. In the Kröger-Vink diagram the same slopes arise for the ionic point defects, i.e., 0, and $\pm\frac{1}{2}$ for the electronic defects, i.e., Equations (5.28) and (5.30). Due to the space charge effect the ranges of validity are different. In the present example a positive space charge potential has been assumed, which implies accumulation of V_M' and e' , and depletion of M_i' and h' .

The model has been used to calculate the point defect profiles as a function of component activity and temperature for the multicomponent system AgCl-Al₂O₃.

For an acceptor-doped metal oxide, Maier presents a qualitative Kröger-Vink diagram assuming a positive space charge potential. Here, the extrinsic regime is increased due to depletion of e' and accumulation of V_O'' .¹⁵⁶ At low P_{O_2} values the curves are approaching the bulk behavior. This particular situation is observed for SnO₂ in O₂ ambients, and has been used to discuss the sensing behavior of SnO₂ in a Taguchi sensor.

FIGURE 5.6. Kröger-Vink diagrams of MX with Frenkel disorder (— = bulk, --- = boundary layer).

A large number of problems in solid state electrochemistry are determined by the defect chemistry in boundary regions rather than in the bulk. Taking the defect chemistry in space charge layers into account, unusual partial pressure dependences of electronic conductivity, which cannot be understood in terms of bulk defect chemistry, can be made plausible. Göpel and Lampe¹⁵⁷ observed for acceptor-doped ZnO, with a defect chemistry quite similar to SnO₂, an accumulation layer for e' and as exponents for the P_{O_2} dependence of the conductivity -0.25 (bulk) and -0.15 ± 0.03 (space charge layer). The bulk value is easily explained by a constant ionic point defect concentration in the acceptor regime.

If a strong depletion of oxide ion vacancies occurs in the space charge layer, electrons should form the majority carriers there. Maier¹⁵⁶ found under these conditions and under the assumptions that no frozen-in profiles exist and a low mobility for the acceptor impurities, for the P_{O_2} dependence of the space charge conductivity theoretically the exponent $-1/8$, which is concordant with the experimental value.

III. CONCLUDING REMARKS

Defect chemistry is a chemistry within the solid state that is analogous to the long-familiar chemistry in the liquid phase, and arises from departures from the ideal crystal structure which are thermodynamically unavoidable, the point defects. While defect chemistry foundations were established over 60 years ago, this area of chemistry enables one to date to

describe in a unified manner a wide variety of phenomena, based on the dynamical behavior of ionic and electronic species, in electroceramics, MIECs, chemically active ceramics, optoceramics, photographic materials, scale growth on metals, and many more.

It has been demonstrated that the classical equilibrium defect chemical concepts derived for binary compounds can be applied to ternary and multinary compounds. In the case of multicomponent materials, the space charge effects will become very important in cases in which the dimensions are no longer large compared with the thickness of the space charge layers, as in extremely thin films or in structural and functional ceramics with crystallites of nanometer dimensions. The formation of latent images in silver halide photography represents a prelude to effects of point defects in nanostructured materials, and is related to enlarged concentrations of point defects in boundary layers.

To date the development of nanostructured materials is receiving widespread attention, and it is believed that classical defect chemical concepts will contribute to the pace of advance in our understanding of improved or new properties of either single-phase or multiphase materials. With regard to multiphase materials the ceramic-metal composites (cermets) with percolation-type conductivity behavior like YSZ-Pd or BaCeO₃-Pd, which exhibit enhanced diffusion of oxide ions and protons, respectively, represent a novel class of gas-separation membranes. While mixed oxide, proton, and electronic conductivity may occur in these cermets, the mechanisms of mass and charge transport will largely be governed by the dynamical behavior of ionic point defects. Hence, classical defect chemistry is invaluable for the field of solid state electrochemistry.

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