4. Impurities and dopants

Introduction

In the preceding chapter we have mainly dealt with pure, crystalline metal oxides, and little account was taken of impurities and dopants and their effects on defect equilibria. Under real conditions it is impossible to produce truly pure crystals and for many oxides impurities may, depending on their concentration and the temperature, significantly affect or fully control defect concentrations in crystals. In the same terms dopants are purposely added to obtain or tailor defect-dependent properties of metal oxides and other materials.

The term dopant is from semiconductor science traditionally used for amounts of foreign atoms in the parts per million (ppm) range. However, many use it, as we shall here, also for foreign atoms in any concentration, up to several or even tens of percent. When one type of atoms is deliberately replaced to any degree by another type of atom, we may also use the term substitution and substituent instead of doping and dopant.

Impurities and dopants may have various effects on crystals. Interstitially dissolved foreign atoms will normally affect the strain in the lattice. When ionised their charge affects the electroneutrality condition. Substitutionally dissolved impurities or dopants will also affect the properties of the host compound if they exhibit a difference in size or charge compared with the host atoms they replace.

In the following we will mainly consider cases where there is a difference in the valence between the foreign atom and the native atom it replaces. Such foreign atoms are termed *aliovalent* or *heterovalent*. Their effective charge will affect the electroneutrality condition and thereby the defect equilibria.

Larger dopant concentrations are generally expected to change also enthalpies of defect formation. However, we shall neglect such effects here and, as a first approximation, treat all cases as ideal dilute solutions, as we have done for defect equilibria earlier.

By the solubility of foreign atoms we mean the amount that can be held by the structure without precipitation of a second phase. This is thus the amount dissolved in equilibrium with that second phase. The solubility of foreign atoms obviously changes with temperature. Less recognised is the fact that the solubility under some defect structure situations also may vary with component (oxygen or metal) activities, as we shall see later.

On account of this it is important to distinguish between the following cases:

1) The concentration of impurity or dopant (solute) is **frozen in**. This is the case at relatively **low temperatures**; too low to allow transport to and from sinks and sources of the foreign atoms (a solute-rich phase). In this

case the **concentration of solute is constant**. We may list some subcases of this situation:

a) If the frozen concentration of solute is below the solubility limit, and no second phase is present, the system is then stable.

b) If the concentration of solute is below the solubility limit, but a second solute-rich phase is present, the system is metastable.

c) If the frozen concentration of solute exceeds the solubility limit, the system is metastable – a common case.

2) The concentration of impurity or dopant (solute) is in **equilibrium**. This is the case at relatively **high temperatures**; high enough to allow transport to and from sinks and sources of the foreign atoms. This case can be divided into two subcases:

a) The total amount of solute present is below the solubility limit. In this case there is no solute-rich phase present, and the concentration of solute is therefore again **constant**, as in all the cases 1).

b) The total amount of solute present is above the solubility limit. In this case there is a solute-rich second phase present, and the concentration of solute is **variable** by exchange of solute between the bulk and the sink/source of second phase.

In science and technology employing solid solutions (alloys or doped systems) it is often assumed that a constant concentration of solute is present. Furthermore, this is often assumed to be constant because it is fully soluble (case 2a), while it may in reality be constant because it is frozen in (cases 1).

During synthesis, sintering, equilibration, and use at high temperatures the concentration may change (case 2b) and this of course is also the basis for binary and higher phase diagrams. Defect chemistry offers a tool for understanding these changes, not only as a function of temperature, but especially as a function of component activities.

Despite this possibility, also defect-chemical treatments most commonly assume that the concentration of dopants and impurities is constant, often (tacitly) because they are assumed to be fully soluble (case 2a)). In reality, this may have been true at the high temperatures used during synthesis and fabrication, while during characterisation or use at lower temperatures the concentrations remain constant rather because they are frozen in (cases 1)). We shall start our treatment with cases of invariable concentrations of aliovalent foreign substituents, disregarding whether this is a result of full solubility or freezing-in.

Constant concentration of impurity/dopant

Schottky equilibria

As the predominance of Schottky defect situations have primarily been demonstrated in detail for ionic halides, e.g. alkali halides (NaCl, KBr, LiI a.o.), let us consider the effects of impurities/dopants on Schottky equilibria in a compound MX where the cations and anions have a valence of 1 and the cation and anion vacancies are singly charged, i.e. $v_X^\bullet$ and $v_M^/$. If divalent foreign cations, Mf^{2+}, are dissolved substitutionally in the lattice and occupy the normal M-sites, the Mf^{2+} ions will have one effective positive charge, $Mf_M^\bullet$. (It has donated an electron, and Mf is called a donor dopant). If we disregard other native defects than the Schottky defects, the electroneutrality condition becomes

$$[Mf_M^\bullet] + [v_X^\bullet] = [v_M^/] \tag{4.1}$$

The defect structure accordingly has two domains given by the limiting cases of this expression:

If the foreign cation is a minority species, i.e., $[Mf_M^\bullet] << [v_X^\bullet]$ then $[v_X^\bullet] = [v_M^/]$, and from the Schottky equilibrium

$$K_S = [v_X^\bullet][v_M^/] \tag{4.2}$$

we obtain

$$[v_X^\bullet] = [v_M^/] = K_S^{1/2} \tag{4.3}$$

If, on the other hand, $[Mf_M^\bullet] >> [v_X^\bullet]$ then

$$[v_M^/] = [Mf_M^\bullet] \equiv constant \tag{4.4}$$

,i.e., the metal vacancy concentration is fixed by the concentration of the foreign cation. The concentration of the minority species, $[v_X^\bullet]$, can be found by insertion into K$_S$:

$$[v_X^\bullet] = \frac{K_S}{[Mf_M^\bullet]} \qquad (4.5)$$

We observe that this concentration decreases with increasing concentration of dopant, as expected also from direct inspection of the electroneutrality condition.

The two regions and their transition is illustrated in the figure below. The region dominated by intrinsic disorder is often called intrinsic, as opposed to the one dominated by foreign species such as dopants or impurities, which is called extrinsic.
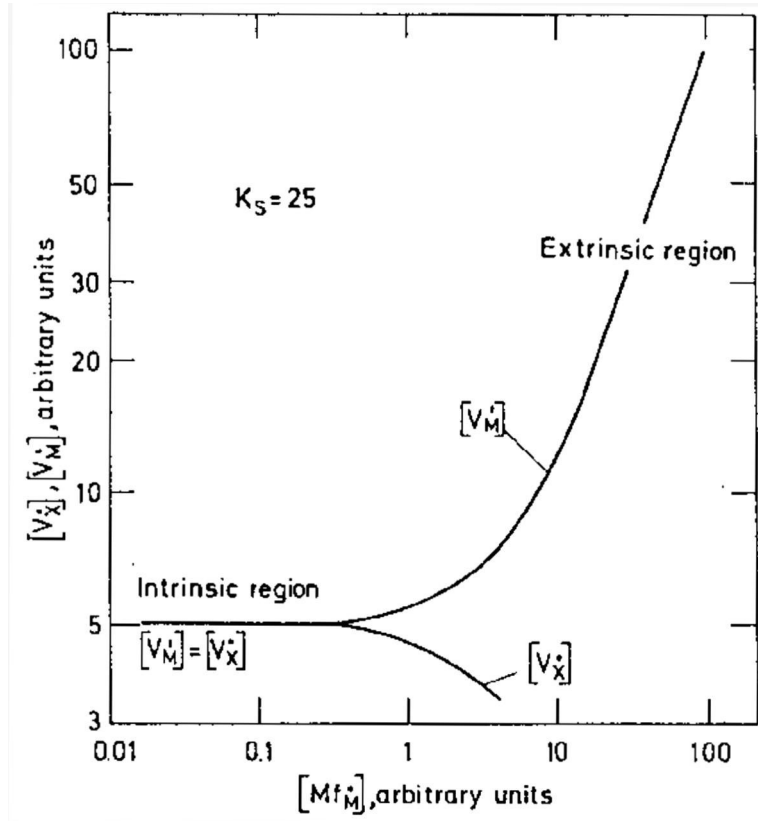

Figure 4-1. Effect of higher valent cation impurities on the defect concentrations in MX predominantly containing Schottky defect pairs, with K_S = 25.

Frenkel equilibria

The effects of higher valent cation impurities on Frenkel equilibria are analogous to those described for the Schottky equilibria. When divalent $Mf_M^\bullet$ impurities/dopants are dissolved in MX with predominating cation Frenkel defect pairs ($v_M^/$ and $M_i^\bullet$) the electroneutrality condition is given by

$$[Mf_M^\bullet] + [M_i^\bullet] = [v_M^/] \qquad (4.6)$$

The addition of $Mf_M^\bullet$ decreases $[M_i^\bullet]$ and increases $[v_M^/]$ in a manner analogous to that described for the Schottky-dominated material.

Oxygen-deficient oxides doped with lower valent cations

A situation which is frequently encountered in applications of several oxide systems is that doubly charged oxygen vacancies are the predominating native point defects – compensated by electrons – and that the cation impurities/dopants have a valence lower than that of the parent cation (impurities/dopants with negative effective charge are also called acceptors). An example is zirconia (ZrO_2) doped with lower valent cations such as for instance yttrium ($Y_{Zr}^/$) or calcium ($Ca_{Zr}^{//}$). For the sake of illustration let us assume that the impurity/dopant ions have one effective negative charge, $Mf_M^/$. The defect equilibrium between vacancies and electrons is as before given by

$$O_O^x = v_O^{\bullet\bullet} + 2e^/ + \tfrac{1}{2}O_2(g) \tag{4.7}$$

$$K_{vO}^/ = \frac{[v_O^{\bullet\bullet}]}{[O_O^x]}\mathrm{n}^2 p_{O_2}^{1/2} \tag{4.8}$$

The electroneutrality condition will be given by

$$2[v_O^{\bullet\bullet}] = [Mf_M^/] + n \tag{4.9}$$

For such a system two limiting conditions can be considered:

If $2[v_O^{\bullet\bullet}] \approx n \gg [Mf_M^/]$, the foreign cations do not affect the native defect equilibrium, and the electron and oxygen vacancy concentrations are given by their own equilibrium, and they are proportional to $p_{O_2}^{-1/6}$ as we have shown in the preceding chapter. This will occur at relatively low oxygen activities, where these concentrations are relatively large.

If $2[v_O^{\bullet\bullet}] \approx [Mf_M^/] \gg n$, the oxygen vacancy concentration is determined and fixed by the dopant content (extrinsic region). The concentration of minority electrons, n, is in this case given by

$$n = (2K_{vO}^/)^{1/2}[Mf_M^/]^{-1/2} p_{O_2}^{-1/4} \tag{4.10}$$

and thus decreases with a different dependency on p_{O_2} than in the former case. As the concentration of electrons and electron holes are related through the equilibrium $K_i = np$, the electron hole concentration in this extrinsic region correspondingly increases with increasing oxygen activity. Depending on the impurity content, oxygen activity and temperature, p may become larger than n.

The variations in $[v_O^{\bullet\bullet}]$, n and p as a function of the partial pressure of oxygen, are schematically illustrated for such a case in the figure below. In a situation like this the oxide will typically be an n-type electronic conductor at low oxygen partial pressure and an essentially ionic conductor at higher oxygen partial pressure. Zirconia doped with a lower valent cation such as Y, Ca, a.o., confers largely with the situation depicted in the figure.
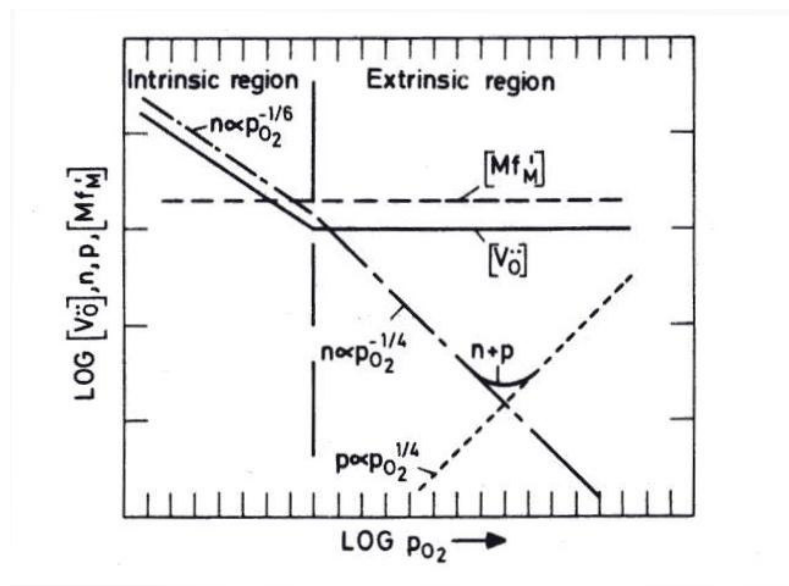

Figure 4-2. Brouwer plot of the concentrations of defects as a function of oxygen partial pressure in an oxygen deficient oxide predominantly containing doubly charged oxygen vacancies, showing the effects of a constant concentration of lower valent cation dopants, $[Mf_M^{/}]$.

Oxygen deficient oxides doped with higher valent cations

Addition of higher valent cations which dissolve substitutionally in the oxide will in the extrinsic region result in an increase in the concentration of electrons and a decrease in the concentration of oxygen vacancies. This may be shown by setting up the appropriate electroneutrality condition combined with the defect equilibria in the same manner as shown above.

Oxides with excess metal

Nonstoichiometric oxides with excess metal in the form of predominating interstitial metal ions exhibit the same qualitative effects of aliovalent foreign

cations. By additions of lower valent cations, the concentration of interstitial cations will in the extrinsic region be determined by the concentration of the impurities/dopants. Addition of higher valent cations will bring about an increase in the electron concentration and a decrease in the concentration of metal interstitials.

Metal-deficient oxides doped with lower valent cations

When a metal-deficient oxide MO with singly charged metal vacancies as the prevalent native point defects is doped with singly valent foreign cations, $Mf_M^{/}$, the electroneutrality condition is given by

$$[v_M^{/}] + [Mf_M^{/}] = p \qquad (4.11)$$

The effects of the foreign cations are evaluated by combining this with the equations for the defect equilibria for the singly charged metal ion vacancies. As a result we find that the lower valent cations will increase p and decrease $[v_M^{/}]$. The variations in p and $[v_M^{/}]$ as a function of the partial pressure of oxygen in such a case are illustrated schematically in the Brouwer diagram below. At low oxygen activities interstitial metal ions or oxygen vacancies may become important, depending on the equilibrium constants for the Frenkel and Schottky defect equilibria. In the figure it is assumed that singly charged metal interstitials become the important native point defects at low oxygen activities.

Figure 4-3. Effect of a constant concentration of foreign lower valent cations on the concentration of point and electronic defects as a function of oxygen pressure in a metal deficient oxide predominantly containing singly charged cation vacancies.

Metal deficient oxides doped with higher valent cations

If the foreign cation impurities/dopants are higher valent, e.g. $Mf_M^{\bullet}$, the electroneutrality condition of an oxide MO with predominantly singly charged metal vacancies becomes

$$[v_M^{/}] = [Mf_M^{\bullet}] + p \tag{4.12}$$

In this case $[v_M^{/}]$ will increase and p will decrease with increasing concentration of $Mf_M^{\bullet}$. The variations in p and $[v_M^{/}]$ as a function of the oxygen partial pressure is illustrated schematically in the following figure, and the variation in the concentration of electrons (n) as minority defects is also included.
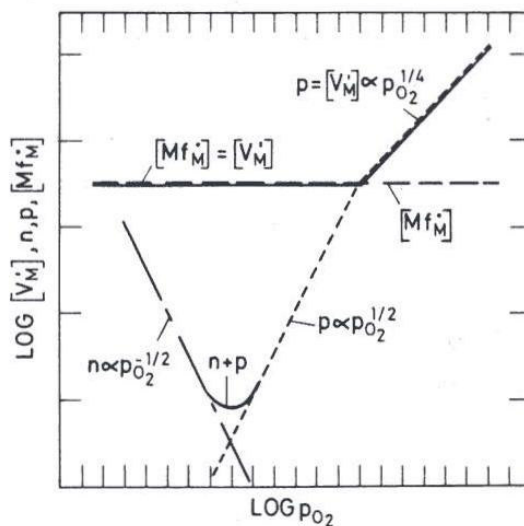
Figure 4-4. Brouwer diagram of the effects of a higher valent cation impurity/dopant on the concentration of point and electronic defects as a function of oxygen pressure in a metal deficient oxide predominantly containing singly charged metal vacancies.

Doping of oxides which may have regions with both oxygen and metal deficit

In the previous examples of the effects of lower valent oxides we have separately considered oxides which are either oxygen or metal deficient. We have seen that the doping is compensated by increased concentrations of either electronic defects or point defects, depending on the type of non-stoichiometry originally present. In principle it is straightforward to combine these treatments and consider the effects of aliovalent foreign atoms over the entire range of stoichiometry, from the oxygen-deficient to the metal-deficient side. Depending on oxygen partial pressure, the doping will be compensated by an electronic

defect or a point defect of the opposite effective charge of the dopant. As we shall see it may be necessary to consider both possibilities when we deal with oxides near stoichiometry.

Let us therefore start with an example oxide M_2O_3 dominated by intrinsic electronic disorder when stoichiometric, and oxygen vacancies and metal vacancies giving oxygen and metal deficiency at, respectively, low and high oxygen activities. We acceptor-dope this oxide with the lower-valent Ml^{2+} cations, such that the electroneutrality condition reads:

$$n + [Ml_M'] + 3[v_M'''] = p + 2[v_O^{\bullet\bullet}] \tag{4.13}$$

We assume that the amount of MlO added is well below the solubility so that $[Ml_M']$ = constant. Figure 4-5 shows a Brouwer diagram of the defect situation as a function of oxygen partial pressure when the level of aliovalent dopant is higher than the level of intrinsic disorder. At the lowest p_{O_2} the oxide is oxygen-deficient and oxygen vacancies and electrons predominate. As these defects decrease with increasing p_{O_2} we hit the level of the acceptor dopant. From here on the acceptor will be compensated by a constant concentration of the positive defect, i.e., the oxygen vacancies. This is analogous to the situation we obtained when we earlier considered this case in particular.

In this situation the concentration of defect electrons decreases and that of holes increases with increasing p_{O_2}. The two terms cross at $n = p = K_i^{1/2}$, and assuming that K_i is independent of the doping, this is necessarily the same level as that of the intrinsic electronic disorder in the pure, undoped material. At this point also the doped material may be said to be stoichiometric; it contains oxygen vacancies exactly matching the presence of the lower-valent cation (acceptor): If we consider the doped material to consist of M_2O_3 and MlO, both these constituents are stoichiometric, and the additional presence of reduced and oxidised states (n and p) is effectively zero at this point. The doped oxide can be said to be stoichiometric with respect to the valence of its constituents.

By further increasing p_{O_2} the concentration of holes will eventually become dominating, taking over the dominance from the oxygen vacancies in terms of compensating the charge of the acceptors. We hereby create higher oxidation states (holes) and fill up the oxygen sublattice (removing oxygen vacancies). During the increase in p_{O_2} the concentration of metal vacancies increases and eventually balances the concentration of oxygen vacancies. This level is given by the Schottky equilibrium constant (K_S) and represents another stoichiometric point, this time with respect to the crystal structure of the host oxide (M_2O_3).

The situation encountered in this region is analogous to that depicted in Figure 4-3, and with further increase in p_{O_2} the charge due to the increasing concentration of metal vacancies will become more important than that of the acceptor level, and the oxide enters into a situation of dominance by metal deficiency.

Figure 4-5 is constructed by combination of limiting cases of the electroneutrality condition (Eq. 4.13) and defect equilibria in a similar manner as we have practised earlier.

It turns out by inspection of several cases that acceptor doping always leads to a region at relatively low p_{O_2} where we have compensation by a positively charged point defect and a region at relatively high p_{O_2} where we have compensation by electron holes. This is true independent of type of intrinsic disorder. However, the relative magnitudes of the equilibrium constants for intrinsic disorder (e.g. K_i vs K_S) determine the relative width of dominance for the two regions.
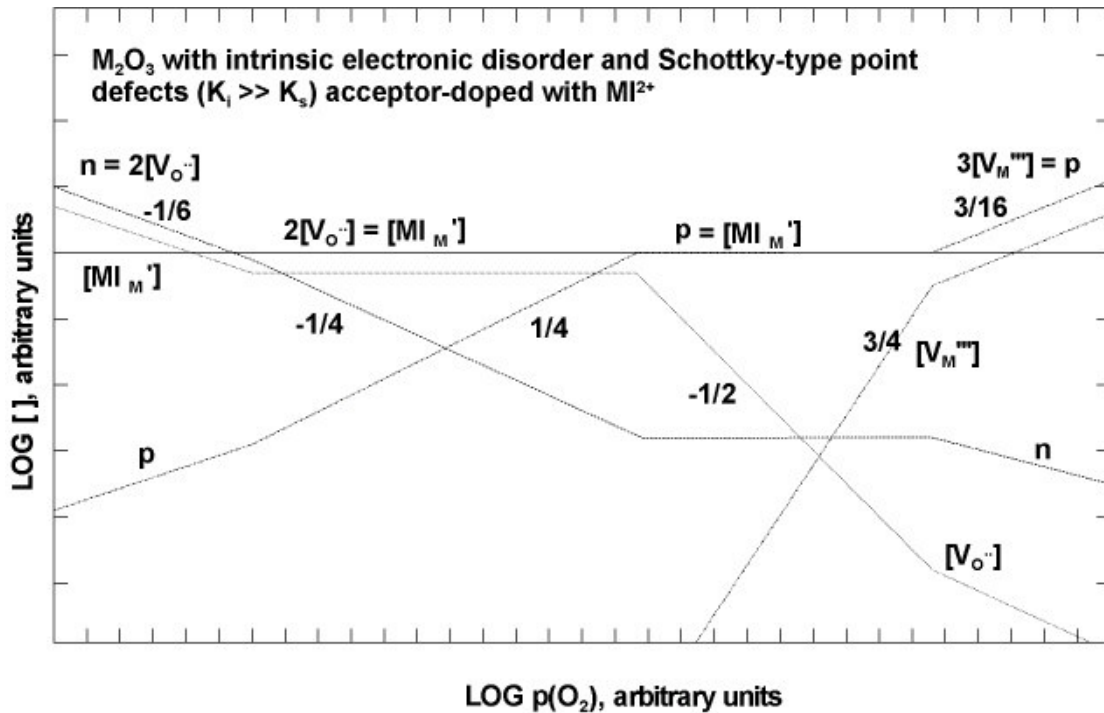
Figure 4-5. Brouwer diagram of the effects of lower valent dopant on the defect structure of $M_2O_{3\pm\delta}$.

In a manner equivalent to the above case we may construct a diagram showing the situation in the same host oxide M_2O_3 now donor-doped with a higher valent cation Mh^{4+} see Figure 4-5. In this case and in all cases of donor-doping, there will be a region of charge compensating the dominating donors with defect electrons at relatively low p_{O_2} and with a negatively charged point defect at higher p_{O_2}
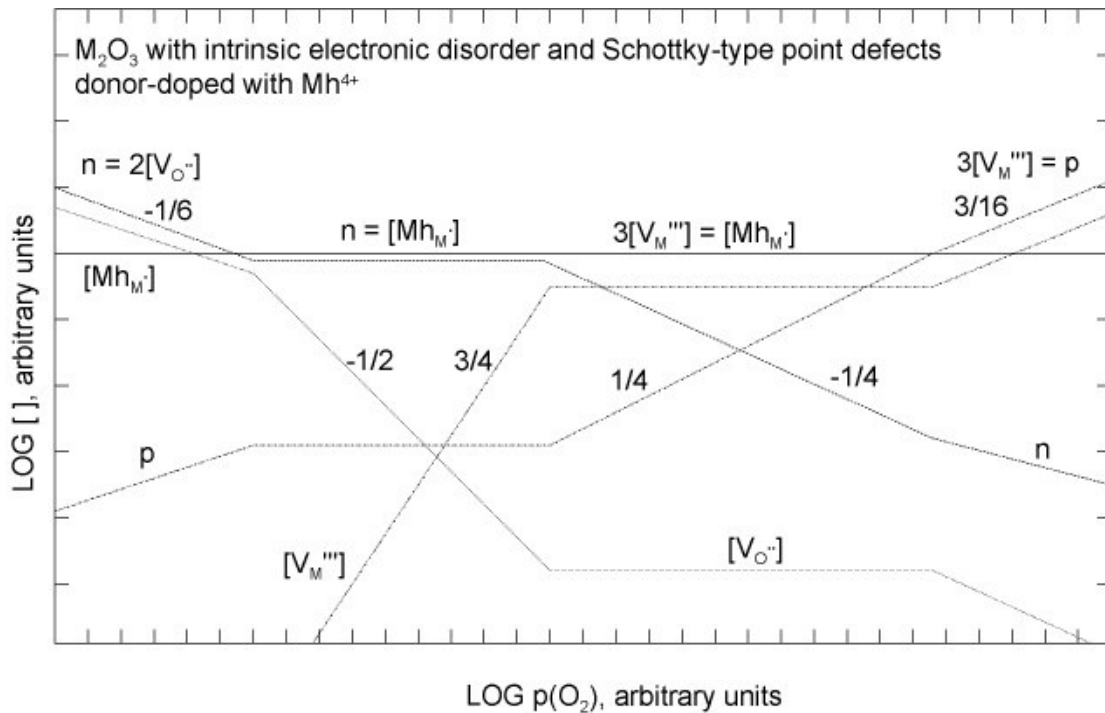
Figure 4-6. Brouwer diagram of the effects of higher valent dopant on the defect structure of $M_2O_{3\pm\delta}$.

We have here concentrated on changes in charge compensation as a function of oxygen activity, but the same may take place as a function of temperature and concentration of dopant (at constant p_{O_2}).

Aliovalent doping affects defects with higher number of charges more than those with fewer. Thus, with increasing doping, doubly and higher charged point defects may become dominating at the expense of the singly charged electronic defects, but not vice versa.

Variable concentration of impurity/dopant

In many cases an impurity or dopant may be present in amounts larger than the solubility limit. The excess of the oxide of the impurity or dopant is then presumably present in precipitates, often found at grain boundaries or surfaces of the parent oxide. When one considers the effects of impurities/dopants on defect equilibria in such cases, it is important to recognise that the solubility of the impurity or dopant will not only vary with temperature but in many cases also with the oxygen pressure. Let us illustrate these aspects by respectively considering the effects of the lower valent oxide MlO and the higher valent oxide MhO_2 on M_2O_3.

Doping M_2O_3 with excess MlO

When Ml dissolves substitutionally in M_2O_3, the dissolved Ml^{2+} has one negative effective charge, Ml_M'. Let us further assume that these ions constitute the important negative effective charges in the oxide. These must then be compensated by positive defects, and let us assume that these are electron holes and doubly charged oxygen vacancies, depending on the properties of the oxide, the temperature, and the oxygen activity.

If the compensating defects are electron holes when MlO dissolves in M_2O_3, the defect equation for the dissolution may be written

$$2\text{MlO(s)} + \tfrac{1}{2}O_2\,(g) = 2Ml_M' + 2h^{\bullet} + 3O_O^x \tag{4.14}$$
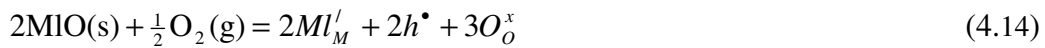
By taking the activity of the excess MlO(s) phase as well as that of oxide ions as unity, the equilibrium expression can be written

$$K_p' = \frac{[Ml_M']^2\,p^2\,[O_O^x]^3}{a_{MlO(s)}^2\,p_{O_2}^{1/2}} = [Ml_M']^2\,p^2\,p_{O_2}^{-1/2} \tag{4.15}$$

The important difference from the previous treatments is that now we treat this dissolution as an equilibrium. When the compensating defects are electron holes, the simplified electroneutrality condition can be expressed by $[Ml_M'] = p$, and by insertion into the equilibrium expression we obtain

$$[Ml_M'] = p = K_p'^{1/4}\,p_{O_2}^{1/8} \tag{4.16}$$

Thus, the solubility, i.e., $[Ml_M']$, increases with p_{O_2} until all MlO is eventually dissolved. Thereafter the behaviour will become as with constant acceptor concentrations (all dissolved or frozen-in), described in Figure 4-5.

When taking into account the defect equilibrium for the formation of oxygen vacancies and the intrinsic electronic equilibrium ($np = K_i$), the concentration of oxygen vacancies is under this situation seen to be proportional to $p_{O_2}^{-1/4}$. At lower oxygen activities the doubly charged oxygen vacancies will thus eventually become the charge compensating defects at the expense of electron holes. In this case it may be more relevant to describe the dissolution of MlO by the following defect reaction and equilibrium expression:

$$2\text{MlO(s)} = 2Ml_M' + v_O^{\bullet\bullet} + 2O_O^x \tag{4.17}$$

$$K_v = \frac{[Ml'_M]^2 [v_O^{\bullet\bullet}][O_O^x]^2}{[M]^2[O]^3 a_{MlO(s)}^2} = \tfrac{1}{12}[Ml'_M]^2[v_O^{\bullet\bullet}]$$

(4.18)

The electroneutrality condition and its combination with the equilibrium then yield:

$$[Ml'_M] = 2[v_O^{\bullet\bullet}] = (24K_v)^{1/3}$$

(4.19)

Thus under these conditions $[Ml'_M]$ is independent of the oxygen activity at equilibrium with the excess MlO(s) phase. Thus, when the dopants are compensated by fully ionised point defects as in this case, the system would behave as if it had no excess or frozen-in dopant concentrations. However, the solubility would change with temperature (through the enthalpy involved in K_v) contrary to the cases without any excess or with frozen-in concentrations.

The overall defect structure situation is illustrated in the Brouwer diagram in Figure 4-7; the important compensating defects are electron holes at comparatively high oxygen activities and oxygen vacancies at low oxygen activities. Both situations will eventually be overtaken by native non-stoichiometry at sufficiently low viz. high oxygen activities.
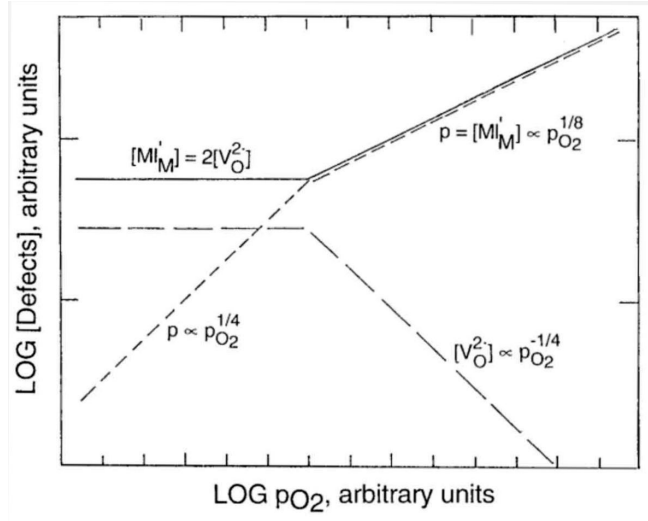

Figure 4-7. Brouwer plot of the effect of lower valent cations, Ml'_M *in M$_2$O$_3$ when the oxide MlO is present in amounts exceeding the solubility limit.*

Doping M$_2$O$_3$ with excess of MhO$_2$

Let us then dope M$_2$O$_3$ with an excess of MhO$_2$. The substitutionally dissolved Mh^{4+} ions have one positive effective charge, $Mh_M^{\bullet}$. They are compensated by defect electrons or point defects with negative effective charge, such as triply charged metal vacancies; $v_M^{///}$.

If the compensating defects are electrons, the reaction equation for the dissolution and the corresponding defect equilibrium are (under certain assumptions, as before) given by

$$2MhO_2(s) = 2Mh_M^{\bullet} + 2e' + 3O_O^x + \tfrac{1}{2}O_2(g) \tag{4.20}$$
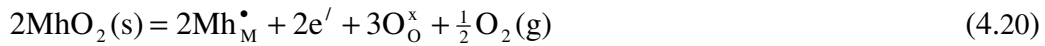
$$K_n' = \frac{[Mh_M^{\bullet}]^2 n^2 [O_O^x]^3 p_{O_2}^{1/2}}{a_{MhO_2(s)}} = [Mh_M^{\bullet}]^2 n^2 p_{O_2}^{1/2} \tag{4.21}$$

Thus, when MhO$_2$ is dissolved by compensation of electrons, the solubility of MhO$_2$ increases with decreasing partial pressure of oxygen. If donor dopants and electrons dominate, the electroneutrality condition and resulting p_{O_2} dependency become $n = [Mh_M^{\bullet}] \propto p_{O_2}^{-1/8}$. Under these conditions it may be shown that $[v_M^{///}] \propto p_{O_2}^{3/8}$.

When the compensating defects at higher p_{O_2} become $v_M^{///}$ the reaction equation for the dissolution of MhO$_2$ can be written

$$3MhO_2(s) = 3Mh_M^{\bullet} + v_M^{///} + 6O_O^x \tag{4.22}$$

Thus, when the dissolution of MhO$_2$ is compensated by the formation of point defects the solubility of MhO$_2$ is independent of the oxygen activity. Under these conditions it may be shown that the concentration of electrons decreases with increasing oxygen activity and is proportional to $p_{O_2}^{-1/4}$. The overall defect structure situation is illustrated by the Brouwer diagram below.
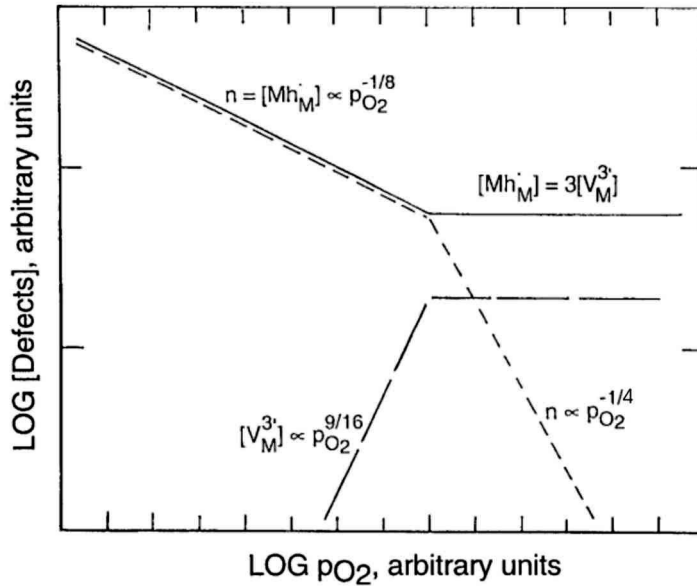
Figure 4-8. Brouwer plot of the effect of the dopant MhO_2 in M_2O_3 in amounts exceeding the solubility limit.

All in all, as a general rule the solubility of lower or higher valent oxides in a parent oxide will be dependent on the oxygen activity when the compensating defects are electronic defects, while they will be independent of the oxygen activity when the compensating defects are fully ionised point defects. It may also be noted that the temperature dependencies of the solubility will also be different in the two cases.

Partially ionised point defects act as combinations of point and electronic defects and generally gives oxygen activity dependent solubilities of aliovalent dopants.

In real cases it may be difficult to reach equilibrium if the diffusion of the cations to and from defect sinks (dislocations, grain boundaries a.o.) is slow. Another point worth mentioning is that the excess second phase may well be a compound of the parent and dopant oxide. For instance, MgO is normally present in excess of the solubility in so-called high-purity alumina (Al_2O_3) and the second phase in that case is spinel $MgAl_2O_4$. However, this does not alter the oxygen activity dependencies; the ternary compound serves as a source/sink for the dopant, with constant activity, and the defect chemical treatment remains essentially the same.

Hydrogen defects in metal oxides

When a metal oxide is equilibrated in gas mixtures with hydrogen-containing gases, e.g. H_2O, hydrogen will dissolve in the metal oxide. The extent

of the dissolution of hydrogen will depend on the defect structure of the oxide and the ambient oxygen and hydrogen activities. In studies of the dissolved hydrogen it is then necessary to control both the oxygen and hydrogen (or water vapour) activities.

Hydrogen may in principle dissolve in the form of different species: as neutral atoms (H), hydride ions (H$^-$), and protons (H$^+$). In oxides the commonly observed dissolved hydrogen species are the protons, often termed interstitial protons, $H_i^\bullet$, but in reality always associated with oxide ions as hydroxide groups. If that oxygen sits on a normal lattice site we thus get substitutional hydroxide defects, $OH_O^\bullet$.

A proper treatment of the dissolution of water and defect chemistry of protons in oxides was first given by Stotz and Wagner (1967). Later on, Norby (1987) and others have given extended treatments of hydrogen defect equilibria, and Kreuer (1996) has reviewed protons in materials in general.

The dissolution of protons from hydrogen gas (e.g. in a gas mixture of H$_2$+H$_2$O) may in these terms be written

$$H_2(g) + 2O_O^x = 2OH_O^\bullet + 2e^/ \tag{4.23}$$

Assuming that water and hydrogen are in equilibrium through H$_2$ + 1/2 O$_2$ = H$_2$O, the defect reaction may equally well be written with water as the source of the protons:

$$H_2O(g) + 2O_O^x = 2OH_O^\bullet + 2e^/ + \tfrac{1}{2}O_2(g) \tag{4.24}$$
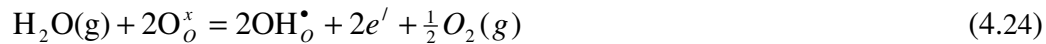
and the corresponding defect equilibrium by

$$K_H^/ = \frac{[OH_O^\bullet]^2 n^2 p_{O_2}^{1/2}}{[O_O^x]^2 p_{H_2O}} \tag{4.25}$$

Thus the concentration of protons in metal oxides is dependent on the partial pressures of both the ambient oxygen and water vapour as well as the concentration of electronic defects.

It may be useful to remind ourselves that water in this context is an oxide present as a second phase in excess and, if we wish, at constant activity (controlled partial pressure). It is thus analogous to the case of an excess of metal oxide. The proton dissolves interstitially forming a positive defect ($H_i^\bullet$ or $OH_O^\bullet$) and thus behaves like a donor: When they are the dominating positive defects in an otherwise undoped oxide they may be compensated by electrons or negative point defects. In analogy with the higher-valent oxide dopant the first case would

lead to a proton concentration dependent on the oxygen activity while it in the latter case would be independent.

As an additional possibility protons may also be compensated by a lower-valent dopant (acceptor). This may, in turn, be present at constant concentration (below the solubility or frozen-in) or itself in equilibrium with its own second phase. In the following examples we will consider some of these relations.

Effect of water vapour on oxygen-deficient M_2O_3.

Let us first examine the effects of water vapour on the properties of an undoped, oxygen-deficient oxide. We will use M_2O_3 in the example, but most of the treatment applies to any oxide. The predominant defects are electrons and oxygen vacancies and the electroneutrality condition in dry environments is then (from the preceding chapter)

$$n = 2[v_O^{\bullet\bullet}] = (2K_{vO}^{/})^{1/3} \, p_{O_2}^{-1/6} \tag{4.26}$$

Let us keep the partial pressure of oxygen constant and vary the partial pressure of the water vapour. Protons are then dissolved in the oxide following Eq. 4.24. However, the concentration of electrons is given by Eq. 4.26 and is independent of p_{H_2O}. Insertion into Eq. 4.25 gives that the proton concentration is proportional to $p_{H_2O}^{1/2}$ (at constant p_{O_2}). This is illustrated in the Brouwer diagram in Figure 4-9.
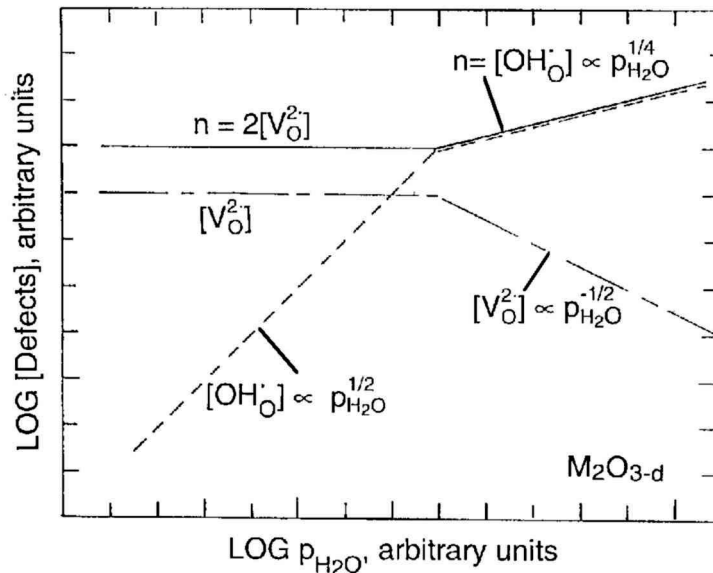

Figure 4-9. Brouwer plot of effects of water vapour on defect concentrations in oxygen deficient M_2O_{3-d}.

At sufficiently high partial pressure of the water vapour, the dissolved protons become the predominating point defects with positive effective charge and the electroneutrality condition becomes

$$n = [OH_O^\bullet] \tag{4.27}$$

By combination with <mark>Eq. 4.25</mark> we obtain that the concentrations of protons and electrons are then proportional to $p_{H_2O}^{1/4}$:

$$n = [OH_O^\bullet] = K_H^{/\ 1/4} \, p_{H_2O}^{1/4} \, p_{O_2}^{-1/8} \tag{4.28}$$

This situation is part of Figure 4-9 above. The figure also shows that the concentration of oxygen vacancies decreases with the water vapour pressure, illustrating that in general all charged native minority defects becoming dependent on water vapour pressure when protons are dominating defects.

Effect of water vapour on acceptor-doped M_2O_3

Let us next consider the effect of water vapour in the oxide M_2O_3 doped with the oxide MlO. Let us further assume that the concentration of the dopant ion $[Ml_M^/]$ is sufficiently large that this is the predominant defect with negative effective charge but that the amount of dissolved MlO is smaller than the solubility limit of MlO in M_2O_3.

In dry atmospheres the dopant ions are assumed to be predominantly compensated by the formation of doubly charged oxygen vacancies ($2[v_O^{\bullet\bullet}] = [Ml_M^/] = \text{constant}$) and under these conditions the concentration of electrons is proportional to $p_{O_2}^{-1/4}$ and the electron holes to $p_{O_2}^{+1/4}$, as derived earlier for this case.

Let us then consider the effect of water vapour on the defect concentrations. For the sake of simplicity let us keep the partial pressure of oxygen constant while the partial pressure of water vapour is increased. Protons then dissolve in M_2O_3 following Eq. <mark>4.24</mark>, and from Eq. 4.<mark>25</mark> it can be derived that the concentration of protons dissolved as hydroxide defects, $[OH_O^\bullet]$, is proportional to $p_{H_2O}^{1/2}$. This is illustrated in Figure 4-9.
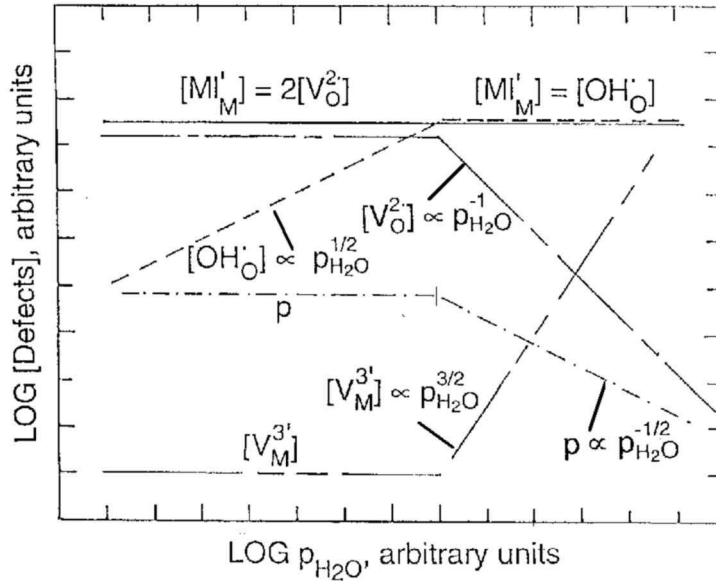
Figure 4-10. Brouwer plot of the effect of water vapour (at constant oxygen pressure) on defect concentrations in acceptor-doped, oxygen deficient M_2O_3.

Under these conditions the electroneutrality includes the concentration of dissolved protons:

$$2[v_O^{\bullet\bullet}]+[OH_O^{\bullet}] = [MI_M^{/}] = \text{constant} \tag{4.29}$$

When we plot the concentration of the defects as a function of the partial pressure of water vapour (at constant oxygen pressure) as shown in the Brouwer diagram in Figure 4-10, it is seen that at sufficiently high water vapour pressures the dissolved protons become the important positively charged point defects and the electroneutrality condition is then approximated by

$$[OH_O^{\bullet}] = [MI_M^{/}] = \text{constant} \tag{4.30}$$

Under these conditions the concentration of oxygen vacancies decreases with increasing partial pressure of water vapour; combining the equilibrium for formation of oxygen vacancies (Eq. 4.8) and the equilibrium for dissolution of protons, Eq. 4.25, and the dominating electroneutrality, Eq. 4.30, it is found that the concentration of oxygen vacancies is proportional to $p_{H_2O}^{-1}$. The concentration of electron holes is correspondingly proportional to $p_{H_2O}^{-1/2}$. These aspects are also illustrated in Figure 4-10.

It is also of interest to consider any effects of the partial pressure of water vapour on the concentration of other minority defects. If so, the ambient partial pressure of water vapour may affect the sintering and creep of metal oxides at

high temperatures. Let us continue to examine the acceptor-doped M_2O_3. For the sake of illustration let us assume that the important defects in the metal sub-lattice are metal vacancies and that these are triply charged, v_M'''. The concentration of oxygen vacancies and metal vacancies in M_2O_3 may be related through the Schottky equilibrium.

In the region where the electroneutrality condition is given by $2[v_O^{\bullet\bullet}] = [Ml_M'] = \text{constant}$, the concentration of the metal vacancies is also independent of the partial pressure of water vapour, cf. Figure 4-10. However, in the region where the electroneutrality condition is $[OH_O^{\bullet}] = [Ml_M'] = \text{constant}$, the concentration of the metal vacancies increases sharply with increasing partial pressure of water vapour and is proportional to $p_{H_2O}^{3/2}$, cf. Figure 4-10. Thus, under these latter conditions the properties which are controlled by the concentration of the minority defects, i.e. sintering, creep, may be greatly affected by variations in the partial pressure of the ambient water vapour pressure. The direction of the change will depend on the effective charge of the rate-limiting defect; whether it is oxygen or metal defects, and whether it is vacancies or interstitials.

When, as in the last example, protons are dissolved at the cost of oxygen vacancies, the reaction may be written

$$H_2O(g) + v_O^{\bullet\bullet} + 2O_O^x = 2OH_O^{\bullet} \qquad (4.31)$$

i.e. water vapour dissolves to fill the oxygen vacancies and replace their positive charge with protons. Reaction 4.31 has been studied for a number of oxides, and it is found that it most often involves a negative enthalpy change such that oxygen vacancies and protons are dominant at high and low temperatures, respectively. For some oxides, the enthalpy is sufficiently negative that protons remain the dominant defects up above 1000°C in practically dry atmospheres and to even higher temperatures under wet conditions. Other oxides have only small negative enthalpies and have dominant protons up to only moderately high temperatures, sometimes sufficiently low to kinetically prevent the reaction with water (Eq. 4.31) to reach equilibrium

The relative dominance of protons vs oxygen vacancies also varies with the acceptor doping level: The higher charge of the vacancy relative to the proton makes the former relatively more dominant at higher acceptor levels, while protons are relatively more dominant at moderate acceptor levels.

Let us also briefly recollect the variable solubility of aliovalent dopants treated previously in this chapter. While the acceptors are compensated by oxygen vacancies, their solubility does not vary with anything else than the temperature, as shown before. However, the dissolution of acceptors by simultaneous dissolution of protons,

$$2MlO(s) + H_2O(g) = 2Ml_M' + 2OH_O^{\bullet} + O_O^x \qquad (4.32)$$
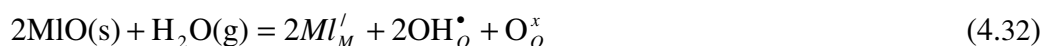
will, when in equilibrium (MlO(s) present and diffusion enabled) give solubility of acceptors which increases with the water vapour pressure:

$$[OH_O^\bullet] = [Ml_M^/] \propto p_{H_2O}^{1/4} \qquad (4.33)$$

Thus, water vapour may in some cases play a role in the synthesis of solid solutions containing acceptors.

By inspection of Figure 4-10 it is evident that at sufficiently high water vapour levels, the concentration of metal vacancies will become significant and eventually dominant; the oxide attains a metal deficiency (or, in other cases, oxygen excess), compensated by protons. Such defect structures can be considered to be the first step towards the phase limit of the oxohydroxide or hydroxide.

Association between impurities/dopants and other point defects

As described in Chapter 1 impurities/dopants and native point defects may associate to form complex defects. An important driving force may be the coulombic attraction between impurities and point defects having opposite effective charges, but also relaxation of the lattice around the associate may play a role.

As an illustration, it will be assumed that the predominating defects are doubly charged oxygen vacancies and that the cation dopants have one effective negative charge, e.g. $Ml_M^/$. The associated complex between $v_O^{\bullet\bullet}$ and $Ml_M^/$ can be written $(v_O Ml_M)^\bullet$, and compared to the relatively mobile oxygen vacancy, this defect can be considered as immobile as the dopant ions themselves.

The complex defect will be in equilibrium with the single defects according to the reaction

$$v_O^{\bullet\bullet} + Ml_M^/ = (v_O Ml_M)^\bullet \qquad (4.34)$$

If all the species are randomly distributed, the equilibrium can be written

$$K_a = \frac{[(v_O Ml_M)^\bullet]}{[v_O^{\bullet\bullet}][Ml_M^/]} \qquad (4.35)$$

where K_a is the equilibrium constant for the association reaction. If the acceptor is relatively immobile, the associated oxygen vacancy can be considered trapped; it is no longer able to contribute in charge or diffusional transport of oxygen, unless an extra activation energy is supplied to break up the association.

Many other alternative examples of the effects of impurities/dopants on defect equilibria may be cited, including association between acceptors and protons, acceptors and holes, donors and point defects, and donors and electrons.

Summary

Impurities or dopants may dissolve interstitially or substitutionally, and the defects formed are often easily ionised. Depending on whether they accept or donate electrons they become acceptors and donors. In sufficient quantities these may dominate the defect structure of the oxide. Thus, aliovalent cations substituting host cations are often introduced in large quantities in oxides in order to give high concentrations of ionic defects (for solid electrolytes) or electronic defects (for electrodes etc.) Foreign species may be treated like other defects, but are often assumed to be present in a fixed concentration due to the limited availability of the species (full solubility) or because the concentration is frozen-in. However, we have shown that the concentration of foreign species under certain conditions may change as a function of temperature and for some defect structures as a function also of p_{O_2}. Protons dissolved from water vapour is a special case which often has a large influence on the properties of oxides. They form hydroxide groups with the oxide ions of the oxide. These are effectively positively charged and through them the defect structure may become a function of the water vapour partial pressure.

Literature (protonic defects only)

Kreuer, K.-D. (1996) *Chem. Mater.* **8**, 640.

Norby, T. (1987) *Advances in Ceramics* **23**, 107.

Stotz, S. and Wagner, C. (1967) *Ber. Bunsenges. Phys. Chem.* **70**, 781.

Problems

1. Write the doping reaction for the doping of the Schottky-dominated metal halide MX by the higher valent metal halide MhX$_2$. Find the analytical solution expressing the concentration of metal vacancies as a funtion of doping concentration. Sketch also the temperature-dependency of all the defects involved. (Hint: This is the initial illustrative case in the text – use the equilibria from that treatment. Remember that the doping reaction is not assumed to be in equilibrium – the dopant concentration is invariable

as a function of outer parameters (although we allow ourselves to vary it at will).)

2. Sketch a Brouwer diagram (double logarithmic diagram of defect concentrations vs p_{O2}) for an oxygen deficient oxide doped with a substitutional higher-valent dopant.

3. Sketch a Brouwer diagram (double logarithmic diagram of defect concentrations vs p_{O2}) for an oxide $M_{1+x}O$ doped with a substitutional lower-valent dopant.

4. Sketch a Brouwer diagram (double logarithmic diagram of defect concentrations vs p_{O2}) for an oxide $M_{1+x}O$ doped with a substitutional higher-valent dopant.

5. Sketch another Brouwer diagram, this time the double logarithmic diagram of defect concentrations vs *dopant concentration*, for the oxide $M_{1+x}O$ doped with a substitutional lower-valent dopant.

6. An oxide M_2O_3 is dominated by intrinsic electronic disorder in the stoichiometric state, while Schottky disorder is the next largest contributor to defects. Draw a Brouwer diagram showing log defect concentrations as a function of the concentration of lower-valent acceptor dopants. Do the same for the case of higher-valent donor dopants. In both cases cover the range from insignificant doping levels to the level where all possible defect domains are exhausted.

7. An oxide M_2O_3 is dominated by Schottky disorder in the stoichiometric state, while intrinsic electronic disorder is the next largest contributor to defects. Draw a Brouwer diagram showing log defect concentrations as a function of the concentration of lower-valent acceptor dopants. Do the same for the case of higher-valent donor dopants. In both cases cover the range from insignificant doping levels to the level where all possible defect domains are exhausted.

8. An oxide M_2O_{3-d} is doped substitutionally with MlO, and dominated by oxygen vacancies and protons as compensating defects. Derive the full expression for the concentration of protons (and oxygen vacancies) as a function of a fixed dopant concentration and the equilibrium constant for the equilibrium between oxygen vacanciens and protons. Make assumptions and simplifications as necessary, but assume that both vacancies and protons are significant compensating defects.

9. Derive equilibria, electroneutrality, and behaviour for an oxide M_2O_3 dominated by metal vacancies and protons dissolved from surrounding water vapour.

10. Choose an acceptor-doped oxide compensated by oxygen vacancies. Write the reaction equation for the association reaction and its equilibrium constant. Derive the temperature-dependency of the concentration of free, unassociated vacancies. Assume that the entropy change of the reaction is zero, and that the enthalpy change is 50 kJ/mol. What is the fraction of free vacancies at 723 K?

Sorry…no answers to the problems in Ch. 4 at present.