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The effects of dopants on the properties of metal oxides

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Abstract

The effect of aliovalent dopants on the defect chemistry of metal oxides is reviewed. The discussion focuses on the stoichiometric solid solution obtained by combination of the stoichiometric dopant oxide and the stoichiometric host oxide without gain or loss of oxygen. The charge of the dopant centers is then compensated solely by ionic defects. As the oxygen activity is raised above that in equilibrium with the stoichiometric composition the lattice defects are gradually replaced by holes. Conversely, when the oxygen activity is reduced below that in equilibrium with the stoichiometric composition the lattice defects are gradually replaced by electrons. The near-stoichiometric region of a pure metal oxide is replaced by two regions with charge compensation by a product of reduction, e.g. oxygen vacancies or electrons, in the region of lower oxygen activity, and by a product of oxidation, e.g. cation vacancies or holes, in the region of higher oxygen activity. © 2000 Elsevier Science B.V. All rights reserved.

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Materials: BaTiO₃

1. Introduction

Dopants are added to a wide variety of metal oxides in order to modify their properties. The goal in some cases is to create or enhance desirable properties, while in others it is to eliminate or reduce undesirable effects. Examples include: Acceptor-doping of zirconia to enhance its ionic conductivity; acceptor-doping of LaCoO₃ to make highly conducting oxide electrodes for thin film, ferroelectric memories; donor-doping of BaTiO₃ to create conducting grains for boundary-layer capacitors; acceptor-doping of BaTiO₃ to move its range of insulating

properties to lower oxygen activities so that Ni can be used as the electrodes in cofired multilayer ceramic capacitors; acceptor-doping of alumina to make transparent envelopes for high intensity lights, etc. In spite of this wide-spread use of dopants for practical applications, a thorough understanding of the properties to be predicted or available is often incomplete. This chapter will review the systematics of doping in the hope that a better understanding will lead to even more improved materials and products. The discussion will be restricted to substitutional aliovalent cation impurities and their effects on the defect chemistry of metal oxides. Isovalent dopants have no first order effect on the defect chemistry, and the use of anion dopants is extremely rare. It is also important to recognize that many oxides have

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useful properties only because of their naturally-occurring impurity contents, i.e. they come to us from nature already doped.

It will be assumed that oxygen is the only volatile species in the systems under consideration, and that thermodynamic equilibrium involves only equilibration with the ambient oxygen activity. Thus, the cationic concentrations are fixed once the solid solution has been established, and this may result in supersaturation of the dopant concentration at lower temperatures.

The effect of dopants on the elemental semiconductors is simple and well-understood. Thus, when phosphorus, with its five valence electrons, is substituted for silicon, which has only four, the phosphorus replicates the bonding of the silicon, and then has one electron left over. This ‘extra’ electron is only weakly bound to the impurity center and is, thus, able to contribute to conduction at normal ambient temperatures. The doping of compounds is somewhat more complex, and that will be the subject of this chapter.

It is hoped that this exposition, tutorial in nature, will be seen to at least approach the clarity and logic that typified the work of Per Kofstad, an esteemed friend and colleague, whose life and career we celebrate with this volume.

2. Stoichiometric solid solutions

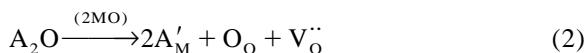
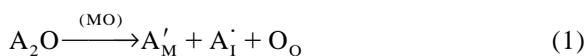
There are several formal routes that can be taken from the starting point of a host oxide and a dopant oxide to reach the final solid solution and its modified properties. One particularly useful route is to consider the solution of one stoichiometric binary oxide into the lattice of another stoichiometric binary oxide, without loss or gain of oxygen. The resulting single phase solid solution can be described as a *stoichiometric solid solution*. In thermodynamic equilibrium, this composition will be stable at only one value of the oxygen activity for any given temperature. For the stoichiometric solid solution, the charge at the aliovalent cation site, relative to that of the perfect lattice, must be compensated for by a lattice defect of the opposite charge in order to preserve bulk charge neutrality. While this is a useful thought process, it is usually not practical. As in the

case of doping TiO_2 with Fe_2O_3 , the two binary oxides will be stoichiometric at different oxygen activities at a given temperature, while the solid solution will be stoichiometric at still a different oxygen activity. We will merely assume that the doping procedure is such that the final product is a stoichiometric solid solution.

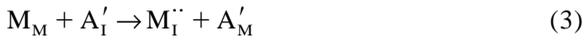
Dopant cations are classified as *acceptor* centers if their charge is less than that of the cation they replace, and *donor* centers if they have a greater charge. These labels recognize that the lattice defect that compensates an acceptor center can be replaced by holes under oxidizing conditions, while the lattice defect that compensates for the excess positive charge of a donor center can be replaced by electrons under reducing conditions. These situations will be discussed later.

The usual Kröger–Vink notation will be used to describe defects; thus an Mg^{2+} ion substituted for a Al^{3+} ion in Al_2O_3 is represented by Mg'_{Al} . It is an Mg ion located on an Al site in the lattice (subscript Al) and has one less positive charge than the ion it replaces (superscript /); an Al^{3+} ion substituted for an Mg^{2+} in MgO is represented by $\text{Al}^{\cdot}_{\text{Mg}}$. It is an Al ion located on an Mg site in the lattice (subscript Mg), and has one more positive charge than the ion it replaces (superscript dot). Dots and slashes are used for these effective defect charges to avoid confusion with the actual electrostatic charge on the species involved. For the sake of generality, the discussion will be in terms of a fictitious oxide of a divalent metals MO, while A^+ and D^{3+} will denote generic acceptor and donor ions, respectively.

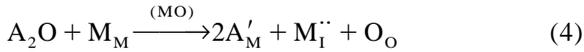
In the stoichiometric solid solution the extra negative charge of an acceptor can be compensated by either a cation interstitial, or an oxygen vacancy.



where it is understood that the dopant oxide replaces the amount of host oxide shown in parentheses above the reaction arrow. In the case of Eq. (1), since the concentration of host cations usually greatly exceeds that of the dopant cations, it may be that the host cation becomes the interstitial species. This can be represented by a cation exchange reaction



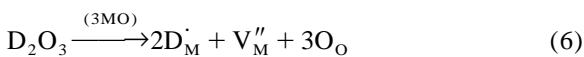
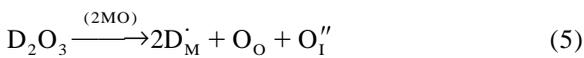
which can be added to Eq. (1) to give an alternative incorporation reaction



Note that these equations explicitly demonstrate the conservation of (1) mass (the same atoms appear on both sides), (2) charge (both sides are charge neutral), and (3) lattice site ratios (the formula MO and the structure require that there be equal numbers of cation and anion sites), as required by the principles of defect chemistry.

In Eq. (2), the replacement ratio is such that the cation sublattice remains perfectly filled, while the anion sublattice is deficient in anions. In Eq. (4), the ratio is such that the anion sublattice is perfectly filled, while the cation sublattice is over-filled. These two limiting cases are always the options; it would be very unusual for compensation to be achieved by a combination of lattice defects. Thus, one type of compensating defect will be greatly favored over the other. The choice will be determined by such factors as ionic radii (large cations or anions may not fit the available interstitial sites) and the charge on the defect. These are the same factors that determine the type of intrinsic ionic disorder favored by a given compound, and it is reasonable that the charge compensating defect be the same as one of the preferred intrinsic defects. Thus in MgO, in which Schottky disorder is the preferred type of intrinsic ionic disorder (V''_M and V''_O), acceptor impurities are compensated by oxygen vacancies.

In the stoichiometric solid solution the extra positive charge of a donor center can be compensated by a cation vacancy or an anion interstitial



Conservation of mass, charge, and lattice site ratios is again apparent. Eq. (5) maintains a perfect cation sublattice, while the anion sublattice is perfect in Eq. (6).

It is useful to demonstrate the dependence of the defect concentrations on the dopant content in a log–log plot. Let us *assume* that the preferred type of

intrinsic ionic disorder in MO is Schottky disorder with its corresponding mass-action expression.



$$[V''_M][V''_O] = K_S \quad (8)$$

where *nil* refers to the perfect lattice. Actually, all conceivable ionic defects are present in amounts determined primarily by their enthalpy of formation, but one type of disorder is almost always sufficiently favored that other types can be neglected. However, this is not the case if some process, such as diffusion, depends on the concentration of a minority defect. Fig. 1 shows both intrinsic and extrinsic regions for donor-doped MO. In the intrinsic region, charge neutrality is approximated by a balance of Schottky defects

$$[V''_M] \approx [V''_O] \quad [D'_M] \ll [V''_O] \quad (9)$$

while in the extrinsic region, it is approximated by a charge balance between the dopant ion, a donor in this case, and the oppositely charged intrinsic defect.

$$[D'_M] \approx 2[V''_M] \quad [D'_M] \gg [V''_O] \quad (10)$$

As the dopant becomes a dominant defect, it carries

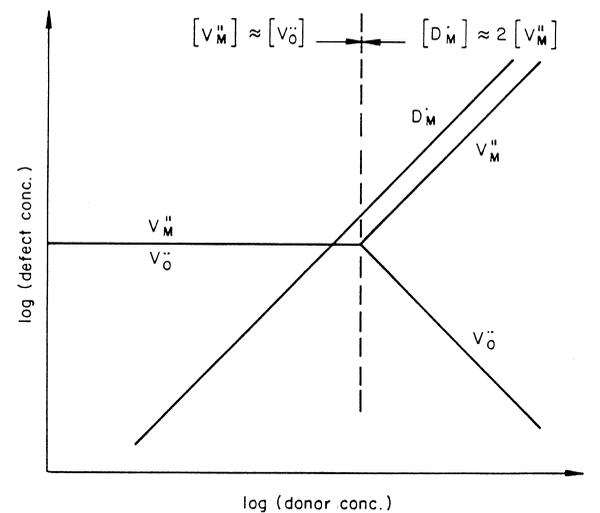
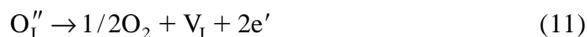


Fig. 1. Defect concentrations as a function of donor impurity content, $[D'_M]$ in the stoichiometric solid solutions of MO. (Reproduced from [1] by permission of Elsevier Science Publishers).

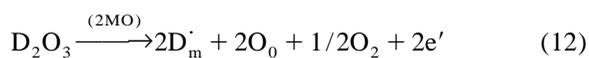
the oppositely charged intrinsic defect up with it to maintain charge neutrality. At the same time, the other intrinsic defect falls away as required by the mass-action expression, Eq. (8). The figure shows why the lattice defect that compensates for the charge of the dopant ion must be one of the dominant intrinsic defects, at least at modest dopant concentrations. There must be continuity of the defect concentrations between the intrinsic and extrinsic regions. It is possible that a minority defect that has a higher power dependence on the dopant concentration could rise fast enough to eventually take over the role of charge compensation, e.g. the anion interstitial's in this example, but this is an extremely rare situation because one rapidly runs out of reasonable space on the log scale of concentration. It should be noted that diagrams such as Fig. 1 are not strictly plots at constant oxygen activity, since in the extrinsic region the oxygen activity in equilibrium with the stoichiometric composition is generally a function of the dopant concentration. They are perhaps better viewed as plots at constant stoichiometry.

3. The shift to electronic compensation

A shift from the stoichiometric solid solution with its compensation by a lattice defect, to a non-stoichiometric solid solution with compensation by an electronic defect, requires an interaction with the ambient atmosphere. The stoichiometric solid solutions may gain or lose oxygen at oxygen activities greater than, or less than, that in equilibrium with the stoichiometric composition. When this process is complete, the compensating lattice defect is eliminated, and is replaced by electrons in the case of donor dopants, or holes in the case of acceptor dopants. For example, for the case of a donor dopant compensated by oxygen interstitials, Eq. (5), it is possible that the lattice excess of oxygen can be lost at low oxygen activities, leaving behind the charge equivalent of electrons



When combined with Eq. (5), this gives a new donor incorporation reaction

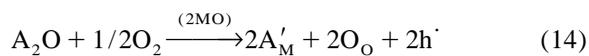


The likelihood of this happening is increased with increasing ease of reduction of the host cation, since this chemical property is reflected in the band structure of the oxide. Examples of this behavior include Ti^{4+} , Nb^{5+} , and W^{6+} , i.e. transition metal ions with empty d levels. The resulting solid solution is now non-stoichiometric, because it has lost oxygen relative to the two binary constituent oxides. Similar results are obtained when the compensating lattice defects are cation vacancies, Eq. (6). In both cases, the replacement of compensating ionic defects by electrons restores the perfect lattice.

Likewise, for the case of an acceptor dopant compensated by oxygen vacancies, Eq. (2), the vacancies may be filled at high oxygen activities, and replaced by the charge equivalent of holes



When combined with Eq. (2), this gives a new incorporation reaction



This mode of compensation is more likely when the host cation is oxidizable. Examples include Fe^{2+} , Co^{2+} , and Ni^{2+} , i.e. transition metal ions in which the filled d levels make up a substantial portion of the valence band states. In the well-known case of NiO doped with Li_2O , i.e. $Ni_{1-x}Li_xO$, compensation of the acceptor centers is by holes, and the material is a good p-type conductor. Once again, the replacement of compensating ionic defects by holes restores the perfect lattice.

In a sense, the nature of the compensating defect in doped oxides depends on the fate of the lattice excess of oxygen, in the case of donor oxides, or lattice deficiency of oxygen, in the case of acceptor oxides. When the perfect lattice is restored by the loss of the excess oxygen in the case of donor-doping, or by the gain of oxygen in the case of acceptor-doping, the charge compensating defects become electrons or holes, respectively.

4. The intermediate stages of non-stoichiometry

The two limiting cases of compensation of aliovalent impurities by ionic or electronic defects are connected by a continuum of non-stoichiometric compositions that have a mixture of ionic and electronic compensation. These can be characterized by equilibrium reactions and mass-action expressions for intrinsic ionic disorder, Eqs. (7) and (8), intrinsic electronic disorder

$$nil \rightleftharpoons e' + h \quad E_g^o \quad (15)$$

$$np = K_I \quad (16)$$

a reduction reaction

$$O_O \rightleftharpoons 1/2 O_2 + V_O \cdot + 2e' \quad \Delta H_N \quad (17)$$

$$\frac{[V_O^{\cdot}]n^2}{[O_O]} = K_N P_{O_2}^{-1/2} \quad (18)$$

an oxidation reaction

$$1/2 O_2 \rightleftharpoons O_O + V_M'' + 2h \quad \Delta H_P \quad (19)$$

$$[V_M''] [O_O]_p^2 = K_P P_{O_2}^{1/2} \quad (20)$$

and an expression for charge neutrality

$$[D_M^{\cdot}] + 2[V_O^{\cdot}] + p = 2[V_M''] + [A_M'] + n \quad (21)$$

The ionic defects have been chosen to be consistent with our assumption that MO prefers Schottky disorder. The mass-action expressions for the four equilibrium defect reactions correspond to three independent relationships, since any one of them can be derived from the other three. The various two-term approximations to the expression for charge neutrality give the fourth relationship necessary to solve for the dependences of the four defect species on the oxygen activity. The results for acceptor-doped MO is shown in the form of a traditional Kröger–Vink diagram in Fig. 2, where the regions of different dependences on oxygen activity are defined by different two-term approximations to the expression for charge neutrality.

In an ideally pure compound, the approximation to charge neutrality in the central part of a diagram such as shown in Fig. 2 would be controlled by the favored type of intrinsic disorder, whether ionic or electronic. However, in most metal oxides the en-

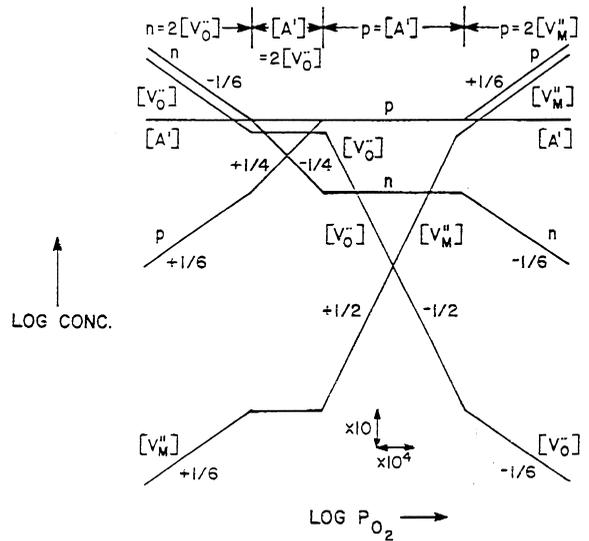


Fig. 2. Kröger–Vink diagram for MO doped with A₂O. It is assumed that the mass-action constant for intrinsic electronic disorder exceeds that for Schottky disorder by a factor of 10⁶. The acceptor concentration causes an increase in the hole concentration by a factor of 10 at the stoichiometric composition. (Reprinted from [2] by permission of Elsevier Science Ltd. Pergamon).

thalpies for all kinds of intrinsic disorder (the enthalpy of Schottky disorder and the band gap in the case of MO) are sufficiently high that the concentrations of naturally-occurring aliovalent impurities exceed those of any type of intrinsic defect. The central part of the diagram is then made up of two extrinsic regions, as shown in Fig. 2. For the case where the dominant impurity is a donor, a diagram such as shown in Fig. 3 is obtained. The compensating defects in the two extrinsic regions are a product of reduction in the region of lower P(O₂), electrons in the case of donor dopants or oxygen vacancies in the case of acceptor dopants, and a product of oxidation in the region of higher P(O₂), cation vacancies in the case of donor dopants or holes in the case of acceptor dopants. The stoichiometric solid solution lies at the value of P(O₂) where n = p at a level that is determined by the band gap. At both ends of the extrinsic regions the diagram reverts to that of the pure compound, as the defects that result from the oxidation and reduction reactions become the dominant defects in the approximations to charge neutrality. The dopants affect the defect

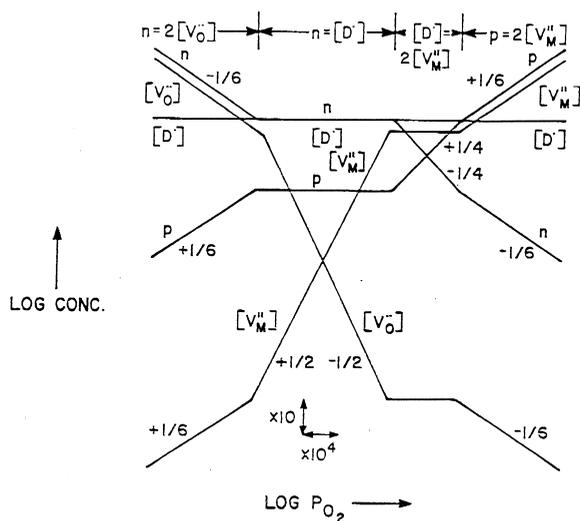


Fig. 3. Kröger–Vink diagram for MO doped with D_2O_3 . It is assumed that the mass-action constant for intrinsic electronic disorder exceeds that for Schottky disorder by a factor of 10^6 . The donor concentration causes an increase in the electron concentration by a factor of 10 at the stoichiometric composition. (Reprinted from [2] by permission of Elsevier Science Ltd. Pergamon).

chemistry only when they are one of the dominant defects in the approximations to charge neutrality.

The presence of extrinsic lattice defects eases the way for the oxidation and reduction reactions under conditions where these reactions can consume some of the defects rather than creating them. Thus, for acceptor-doped MO when oxygen vacancies are the compensating defects the oxidation reaction can fill some of the extrinsic vacancies rather than create cation vacancies.



It is easily shown by combination of the intrinsic oxidation and reduction reactions and their enthalpies that

$$\Delta H_N + \Delta H_p = \Delta H_S + 2E_g^0 \quad (23)$$

For the extrinsic oxidation reaction just described, however,

$$\Delta H_N + \Delta H_{O_x} = 2E_g^0 \quad (24)$$

It is thus apparent that

$$\Delta H_{O_x} = \Delta H_p - \Delta H_S \quad (25)$$

The enthalpy of oxidation has been reduced from that of the ideally pure oxide by the enthalpy of Schottky disorder, usually a substantial quantity.

Likewise, for acceptor-doped MO in the region where holes are the compensating defect, the reduction reaction can proceed by the consumption of part of this large reservoir of holes, rather than by creating electrons



The enthalpy relationship is then

$$\Delta H_{red} + \Delta H_p = \Delta H_S \quad (27)$$

and the enthalpy of reduction has been reduced by twice the band gap, again a substantial quantity. Note the inverse relationship between the extrinsic oxidation and reduction reactions, which indicates that

$$\Delta H_{O_x} = -\Delta H_{red} \quad (28)$$

Thus one of these enthalpies must be negative unless both of them are zero. An example of the behavior just described is seen in Fig. 4 for the well-known case of $BaTiO_3$. Whereas the reduction reaction, Eq. (15) represents no intuitive difficulties, the intrinsic oxidation reaction would require the formation of either interstitial oxygen or both kinds of cation vacancies; neither alternative is very attractive. Yet the enthalpy of oxidation, 0.9 eV is much less than that of reduction, 5.9 eV (for the gain or loss of one oxygen atom, respectively). This reflects the ease of oxidation when there are extrinsic oxygen vacancies available to be filled, and the oxidation reaction then consumes defects rather than creating them.

5. Electronic defects: free or trapped?

Even when a dopant is compensated by an electronic defect, it is not certain that the electrons or holes will result in high conductivities. By definition the dopant and its compensating defect have opposite charges and there is always the possibility that the electrons or holes will be electrostatically bound to the impurity center. Thus in acceptor-doped TiO_2 , the holes that are present at high oxygen activities are strongly trapped by the acceptor centers and do not result in significant conductivity at room tem-

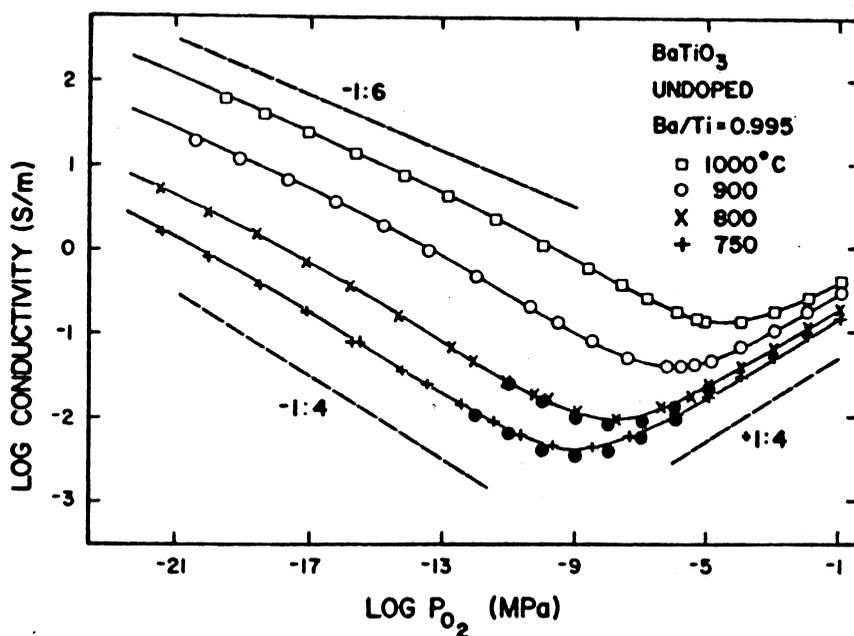


Fig. 4. The equilibrium electrical conductivity of BaTiO_3 doped with 134 ppm Al^{3+} substituted for Ti^{4+} as a function of oxygen activity. Lines with ideal slopes are drawn for comparison. (Reproduced from Ref. [3] by permission of The American Ceramic Society).

perature. On the other hand, donor-doped TiO_2 , in which the compensating defects are electrons under reducing conditions, is a black semiconductor. Acceptor-doped NiO , where holes are the compensating defects, is a well-known p-type conductor, even at room temperature.

A simple predictive rule, based on the chemical properties of the host cation, is useful for understanding these asymmetric doping properties. When the host cation is reducible, but not oxidizable, e.g. Ti^{4+} and Nb^{5+} , donor levels are very shallow, while acceptor levels are relatively deep, usually in the range 0.5–1 eV. These systems are then n-type conductors when donor-doped, but p-type insulators when acceptor-doped. When the host cation is oxidizable, but not reducible, as in the case of NiO , the acceptor-doped material is a p-type conductor. This correlation results from the fact that the electronic states in the solid derive directly from the electronic states of the constituent ions, and retain many of their properties. Since Ti^{4+} is rather easily reduced to Ti^{3+} by placement of an electron in the otherwise empty 3d levels, the nominally empty conduction band in TiO_2 , which is made up primarily of Ti 3d

states, is also receptive to electrons. This results in shallow donor levels.

6. Summary

The properties of doped metal oxides depends on the fate of the excess oxygen, or deficiency of oxygen, brought into the solid solution by the donor or acceptor oxide, respectively. If there is no gain or loss of oxygen from the stoichiometric solid solution, the charged impurity centers are compensated by lattice defects. The latter can be gradually replaced by holes or electrons by oxidation (for acceptor-doped oxides) or reduction (for donor-doped oxides). Oxidation or reduction reactions can be greatly enhanced when the reaction can consume the extrinsic compensating defect rather than generate new defects as is required for ideally pure compounds. Even when the compensating defects are electrons or holes, the product may still be insulating if the electronic defects are strongly trapped by the oppositely charged impurity centers, e.g. holes are strongly trapped in acceptor-doped oxides when the host

cation(s) is(are) not easily oxidized (transition metal cations with empty d-shells), while electrons are strongly trapped in donor-doped oxides when the host cation(s) is(are) not easily reduced (transition metal cations in their lowest available oxidation states, e.g. Mn^{2+} , Ni^{2+} , Co^{2+}).

perature Chemistry: Defect Chemistry of Solids, Elsevier, Amsterdam, 1989, pp. 1–27, Chapter 1.

- [2] D.M. Smyth, The role of impurities in insulating transition metal oxides, *Prog. Solid St. Chem.* 15 (1984) 145–171.
- [3] N.-H. Chan, R.K. Sharma, D.M. Smyth, *J. Am. Ceram. Soc.* 64 (1981) 556–562.

References

- [1] D.M. Smyth, Defects in inorganic compounds, in: Ø. Johansen, A.G. Andersen (Eds.), *Selected Topics in High Tem-*