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Low Temperature Defect Chemistry of Oxides

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Abstract

Defect chemistry at lower temperatures, e.g. room temperature, is systematically described, at which the oxygen exchange reaction is no longer reversible. Analytical relations, numerical results, case studies as well as technological and scientific relevance are highlighted. It is pointed out that the low temperature defect chemistry also offers a quantitative basis to manipulate charge carrier and defect concentrations and related physical properties of oxide electroceramics. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

The oxygen nonstoichiometry, often dominating physical properties and device performance, is established at high temperatures during processing procedures (e.g. sintering and film deposition) or during cooling after the high temperature treatments. On the other hand, many devices and systems based on oxide electroceramics are applied around room temperature. While the (high temperature) defect chemistry can well describe the defect concentrations under complete equilibrium conditions, a quantitative description of defect concentrations at lower temperatures, e.g. room temperature, has seldom been dealt with but is of technological and scientific relevance.[1–8] The transition between the high temperature and low temperature defect chemistry has already been discussed by Kröger *et al.*[1] and applied to the zero Kelvin situations. Waser[2] used this concept explicitly for single-crystalline and polycrystalline $SrTiO_3$. Denk *et al.*[3,4] measured and calculated defect concentrations for ionic and electronic carriers in $SrTiO_3$ within a wide parameter range in such the equilibrium and quenched states. Maier[5] analyzed the situation also in view of the preparation strategy for obtaining a reproducible defect chemistry at lower temperatures. At such low temperatures, oxides are in partially frozen-in states rather than in complete equilibrium with the surrounding atmosphere. Studies in the field of solid state ionics seldom deal with low temperature behavior appropriately, while literature on solid state physics often neglects high temperature equilibration and ionic defects. In this paper, we want to contribute to filling this gap by outlining parts of our systematic research in this respect.[6–8]

2 Defect Chemistry: Complete Equilibrium versus Partially Frozen-in States

In complete equilibrium, all reactions especially the oxygen exchange equilibrium with the surrounding atmosphere are reversible. Using mass action laws, mass and site conservation conditions as well as the electroneutrality condition, the defect concentrations can be determined as a function of state variables and controlling parameters. In partially frozen-in states in which the oxygen exchange equilibrium is no longer reversible, we lose one mass action law but we gain another conservation condition allowing us again to derive defect concentrations (Fig. 1). This additional condition is the constancy of the extent of nonstoichiometry, stating that the oxygen deficiency (in Kröger–Vink notation[1])

$$\begin{aligned} -c_o &= \left[V_o^{\bullet\bullet}\right] + \left[V_o^{\bullet}\right] + \left[V_o^{x}\right] - \left[O_i''\right] - \left[O_i'\right] - \left[O_i^{x}\right] \\ &= \left[V_o^{\bullet\bullet}\right]_E + \left[V_o^{\bullet}\right]_E + \left[V_o^{x}\right]_E - \left[O_i''\right]_E - \left[O_i'\right]_E - \left[O_i^{x}\right]_E \end{aligned} \quad (1)$$

is invariant during cooling from a higher temperature T_E (freezing-in temperature), at which the complete equilibrium has been achieved.[8] For simplicity, we neglected the native cationic defects. The index E denotes the value at $T = T_E$. The

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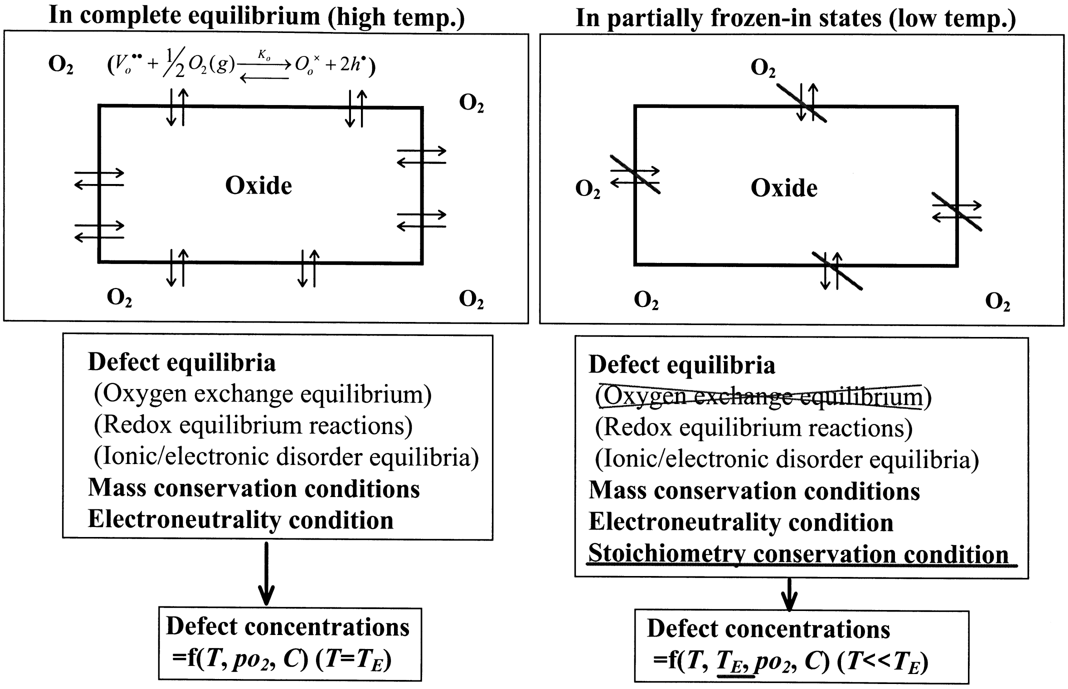


Fig. 1. Defect chemistry: in complete equilibrium versus in partially frozen-in states.

procedure how to fulfill the quenching conditions most accurately is given in Ref. 5.

Since all ionic and electronic defect interactions take place only within the bulk in the partially frozen-in states, we can also state that the sum of the free and trapped holes minus the sum of the free and trapped electrons (S_E) is invariant during cooling as easily shown by combining eqn (1) with the conditions of electroneutrality and mass conservation. In oxides containing a redox-active acceptor (M) exhibiting two valence states ($c_M = [M^{(n-1)\prime}] + [M^{n\prime}] = \text{const}$), this (overall) electronic conservation condition reads:[8]

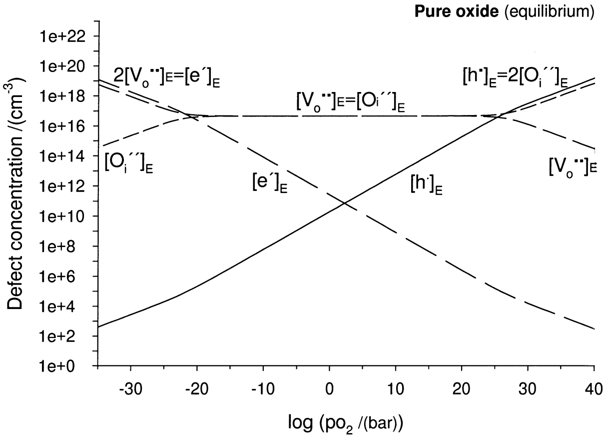
$$\begin{aligned}
S_E &= [h^\bullet] + [(M^{n\prime}\cdot h^\bullet)] + [(O_i''\cdot h^\bullet)] + 2[(O_i''\cdot 2h^\bullet)] \\
&\quad - [e'] - [(V_o^{\bullet\bullet}\cdot e')] - 2[(V_o^{\bullet\bullet}\cdot 2e')] \\
&= [h^\bullet] + \left[M^{(n-1)\prime}\right] + [O_i'] + 2[O_i^x] \\
&\quad - [e'] - [V_o^\bullet] - 2[V_o^x] \\
&= [h^\bullet]_E + \left[M^{(n-1)\prime}\right]_E + [O_i']_E + 2[O_i^x]_E \\
&\quad - [e']_E - [V_o^\bullet]_E - 2[V_o^x]_E
\end{aligned} \tag{2}$$

3 Numerical Calculations: Charge Carrier Concentrations in Partially Frozen-in States

Defect concentrations at lower temperatures, e.g. $T = 25\,°C$, can be calculated by using eqn (1), and by considering the electronic disorder equilibrium, the ionic disorder equilibrium, and the defect ionization equilibria of oxygen vacancies and interstitials as well as of impurity ions. We consider as examples two kinds of (idealized) model oxides: a pure oxide (Fig. 2) and an acceptor-doped [shallow acceptor (A') doped] oxide containing an additional minor redox-active impurity (deep acceptor M' and M'') (Fig. 3). In all cases, we assume dilute conditions. Equilibrium defect concentrations at $T_E = 800\,°C$ are shown in Figs 2(a) and 3(a), while the electron and hole concentrations at 400, 200, and 25°C in partially frozen-in states are shown in Figs 2(b) and 3(b), calculated without further approximations. (Details about the calculation procedure and defect chemical parameters used are given in Ref. 8.) The po_2 in the partially frozen-in states is the po_2 at which the oxides have been equilibrated [$T = T_E$ (800 °C in this study)].

In the pure oxide, two po_2 regimes in the partially frozen-in states [Fig. 2(b)] may be distinguished, separated by the intrinsic po_2 at which $[h^\bullet]_E = [e']_E$. Below this intrinsic po_2, the (major) electron concentration remains almost unchanged, while the (minor) hole concentration decreases rapidly during cooling owing to the electronic equilibrium ($\text{nil} \rightleftarrows h^\bullet + e'$). The minor charge carrier concentration is therefore negligible, as soon as the temperature is reduced. Above the intrinsic po_2, the (major) hole concentration remains almost unchanged, while the (minor) electron concentration is negligible at lower temperatures. In acceptor-doped [shallow acceptor (A') doped] oxides without redox-active impurities, the po_2 regimes

(a) In complete equilibrium (T_E=800°C)



(b) In partially frozen-in states

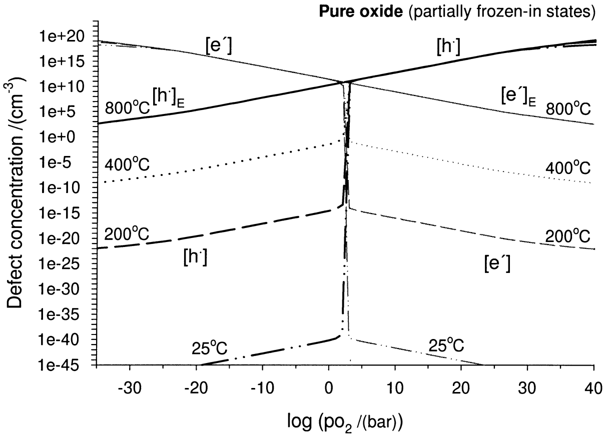
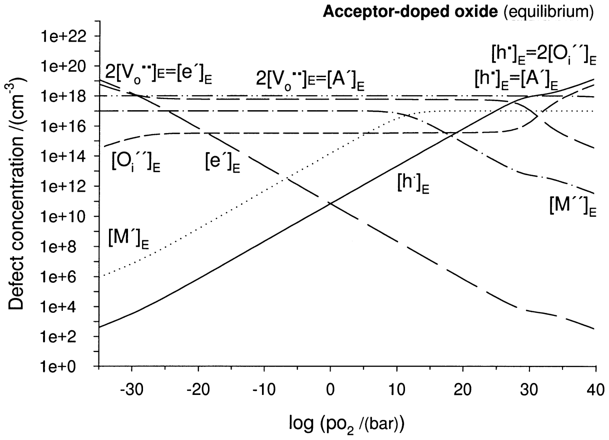


Fig. 2. Defect concentrations in a pure oxide: (a) in complete equilibrium at 800°C and (b) in partially frozen-in states. Defect chemical parameters are taken from Ref. 8. The po_2 in (b) is the po_2 at which the oxide has been equilibrated (T_E = 800°C). The minor modification of the $[h^\bullet]$ and $[e']$ curves occuring at very high and low po_2 are caused by native trapping.

(a) In complete equilibrium (T_E=800°C)



(b) In partially frozen-in states

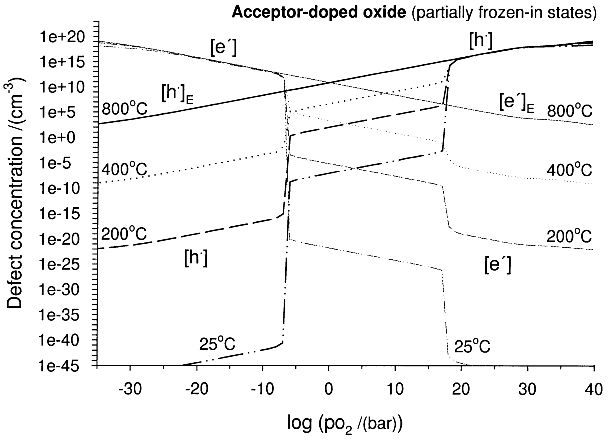


Fig. 3. Defect concentration in an acceptor-doped oxide (shallow acceptor: $c_A = 1 \times 10^{18}$ (cm^{-3}) $\cong [A']$), containing minor redox-active acceptor (deep acceptor: $c_M = 1 \times 10^{17}$ (cm^{-3}) $= [M'] + [M'']$): (a) in complete equilibrium and (b) in partially frozen-in states. Defect chemical parameters are taken from Ref. 8. The po_2 in (b) is the po_2 at which the oxide has been equilibrated (T_E = 800°C).

were similar except that the intrinsic po_2 was shifted to a lower po_2.[8] However, in the acceptor-doped oxide containing a minor redox-active impurity (M), an additional intermediate po_2 regime appears, as can be found in Fig. 3(b). Comparing Fig. 3(b) with Fig. 3(a), one can find that the regime boundaries lie at po_2 at which $[M']_E = [e']_E$ and at po_2 at which $[M'']_E = [h^\bullet]_E$. Within this intermediate po_2 regime, both $[h^\bullet]$ and $[e']$ decrease with decreasing temperature (T). Defect concentrations have been calculated in various types of pure, acceptor-doped, and donor-doped oxides.[8]

4 Analytical Relations

From the ceramic processing viewpoint, it is very helpful to give simple (analytical) relations predicting defect concentrations as functions of processing parameters. Such parameters may include po_2 (at the equilibration at T_E), T (operation temperature of devices), T_E (freezing-in temperature), ΔH_M° (ionization enthalpy, i.e. impurity energy level), and c_M (impurity concentration). It is worth mentioning in this context that the number of oxides with a known complete set of defect chemical parameters, essential for numerical calculations, is still very limited.

Let the hole be the major charge carrier (i.e. $[h^\bullet]_E \gg [e']_E$) and let the redox-active ion M^n be a free trap available for the hole, eqn (2) can be simplified to,[6–8]

$$S_E \cong [h^\bullet] + \left[M^{(n-1)\prime}\right] = [h^\bullet]_E + \left[M^{(n-1)\prime}\right]_E \qquad (3)$$

that is, the sum (S_E) of free holes ($h^\bullet$) and trapped holes $[M^{(n-1)\prime}$, i.e. occupied traps] remains the same in partially frozen-in states. For the oxides containing the redox-active ion M $\left(M^{(n-1)\prime} \overset{K_M}{\rightleftarrows} M^{n\prime} + h^\bullet;\ K_M \equiv [M^{n\prime}] \cdot [h^\bullet] / \left[M^{(n-1)\prime}\right],\ c_M = \left[M^{(n-1)\prime}\right] + [M^{n\prime}]\right)$ under oxidizing conditions, we obtain the following relations describing the hole concentration and the impurity concentrations with specific valence states:[6–8]

$$[h^\bullet] = -\frac{c_M + K_M - S_E}{2} + \sqrt{\left(\frac{c_M + K_M - S_E}{2}\right)^2 + K_M \cdot S_E} \tag{4}$$

$$\left[M^{(n-1)\prime}\right] = \frac{c_M + K_M + S_E}{2} - \sqrt{\left(\frac{c_M + K_M - S_E}{2}\right)^2 + K_M \cdot S_E} \tag{5}$$

$$[M^{n\prime}] = \frac{c_M - K_M - S_E}{2} + \sqrt{\left(\frac{c_M + K_M - S_E}{2}\right)^2 + K_M \cdot S_E} \tag{6}$$

Equations (4)–(6) can be further simplified for cases of interest.[8] For the sake of brevity, let us concentrate on the case characterized by $\left[M^{(n-1)\prime}\right]_E$, $[M^{n\prime}]_E \gg [h^\bullet]_E$ as often encountered in oxides with low electronic concentrations, eqn (4) becomes

$$[h^\bullet] \cong \frac{K_M}{K_{ME}} \cdot [h^\bullet]_E \tag{7}$$

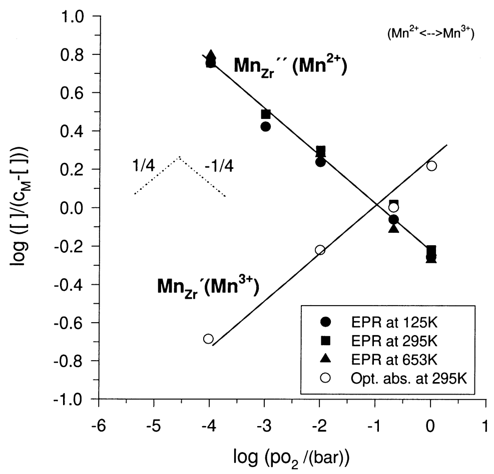
a relation which has already been used in Refs 2 and 3. This relation clearly shows that even though $[h^\bullet] \ll [h^\bullet]_E$, the po_2 dependence is the same as for $[h^\bullet]_E$ (K_M and K_{ME} are po_2 independent). The temperature (T) dependence however is given by the T dependence of $K_M \propto \exp\left(-\Delta H^\circ_M/kT\right)$. Because of the validity of the ionization equilibrium for all temperatures, eqn (7) is identical with the statement that redox ratio $[M^{n\prime}]/\left[M^{(n-1)\prime}\right]$ is invariant with temperature. The dependencies on various other controlling parameters are discussed elsewhere.[8]

5 Case Studies

The partially frozen-in states are often encountered in real situations. Two examples are touched upon here: the concentrations of impurity ions with specific valence states in $ZrO_2(Y_2O_3)$, and the electronic conductivity in Fe-doped $SrTiO_3$ and $SrZrO_3$ (Y_2O_3). Details on experimental results are given elsewhere.[3,6,7,9]

EPR(ESR) and optical absorption spectroscopy are useful (*in situ* and *ex situ*) techniques to directly detect and identify the valence states of redox-active impurities. For examples, several transition metal and rare earth ions have been found to be redox-active in $ZrO_2(Y_2O_3)$ studied by both techniques using selectively-doped single crystals.[6] Figure 4 shows the concentration ratio of Mn_{Zr}'' (Mn^{2+}) and Mn_{Zr}' (Mn^{3+}) in $ZrO_2(Y_2O_3)$. The ratio measured at different temperatures in complete equilibrium (800 °C) was identical to that in partially frozen-in states [Fig. 4(a)] which is a direct verification of eqn (7). Figure 4(b) shows the ratio of the valence states calculated via more general eqns (5) and (6), confirming that the ratio is unchanged during cooling within the po_2 range studied, but also predicting a different situation if the oxide had been annealed at much higher po_2.

(a) measured



(b) calculated

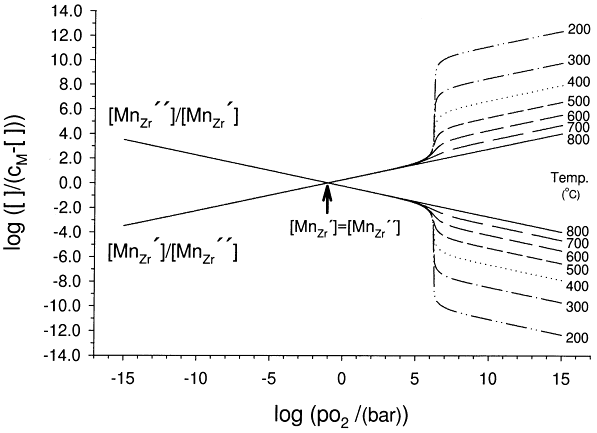


Fig. 4. The redox-state of Mn ions ($[Mn_{Zr}'']/(c_M - [Mn_{Zr}''])$ and $\left[Mn'_{Zr}\right]/(c_M - [Mn_{Zr}'])$) in 9·5 mol% Y_2O_3–ZrO_2 (a) measured by EPR and optical absorption at different temperatures, and (b) calculated via eqns (5) and (6). The po_2 in (b) is the po_2 at which the oxide has been equilibrated ($T_E = 800°C$).

For single crystalline Fe-doped $SrTiO_3$ without any surface modifications, Denk *et al.*[3] have shown experimentally and numerically that the defect chemistry approximately below 750 K corresponded to that for partially frozen-in situations, while, above 750 K, the complete equilibrium with the surrounding atmosphere was achieved within a reasonable waiting period. As a consequence of trapping, ionic conductivity became predominant below 500 K.[2,3,7] The exact agreement of the experimental data with the numerical modeling was set out in Ref. 3. Figure 5 shows the coincidence of numerical and analytical calculations via [eqns (1), (4), and (7)].

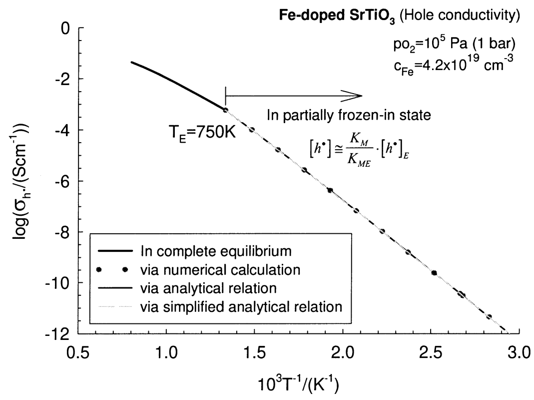


Fig. 5. Hole conductivity in $SrTiO_3$ doped with Fe, calculated numerically [eqn (1)], via the analytical relation [eqn (4)], and via the simplified analytical relation [eqn (7)] which is valid under the experimental conditions chosen. Defect chemical parameters are taken from Ref. 3, and the agreement of the calculations with the experiments was given in Ref. 3.

It is obvious that the neglect of redox-active impurities can lead to serious misinterpretations also with respect to the mechanism of the electronic conduction. In $SrZrO_3(Y_2O_3)$, there are indications that impurity hopping plays an important role. Thus the measured activation energy of the electronic conductivity is very probably due to the ionization enthalpy (e.g. Fe impurity) and not due to a small polaron hopping energy as usually assumed.[7,9]

6 Technological and Scientific Relevance

The low temperature defect chemistry suggests several implications of technological and scientific relevance.[7] At this point, let us just mention one: Because of the fact that the trapping can diminish electronic carrier concentrations in the partially frozen-in states, appropriate dopants (traps) can be used to manipulate the ionic transference number, even if this is not possible in complete equilibrium. In this way, a mixed conductor may be converted into a pure ionic conductor under partially frozen-in conditions. In addition, we have a further degree of freedom by selecting the freezing-in temperature (T_E). On the other hand, measurements of defect concentrations and related properties such as electronic conductivity will yield—in conjunction with such an analysis—defect chemical parameters, e.g. the ionization enthalpies of defects.

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