



Modeling and Characterization of Electrical Transport in Oxygen Conducting Solid Electrolytes

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Abstract. A model for the electrical conductivity in acceptor-doped oxides which involves an association between the acceptor-dopants and oxygen vacancies resulting in donor centers is considered. The model relates the behavior of the electrical conductivity with the temperature, ambient atmosphere and band structure. The predictions of the model are compared to experimental data for $\text{ZrO}_2:16\% \text{Y}$ and $\text{SrCeO}_3:5\% \text{Yb}$ oxygen conductors and some band structure parameters have been determined.

Keywords: ionic conductivity, defects, nonstoichiometry, perovskites, zirconia oxide

1. Introduction

Ionic conductivity in oxides such as ZrO_2 , CeO_2 and SrCeO_3 can be increased by the addition of acceptor dopants. It is well understood that the oxygen vacancies which are formed to charge compensate the acceptors leads to higher ionic transport. Old-fashioned models are based on the assumption that the oxygen vacancies are fully ionized, can move freely in the electrolyte matrix and their number is defined by the acceptor concentration. In this case, the ionic conductivity $\sigma_i = 2e[V_{\text{o}}^{\cdot\cdot}]\mu_{v_{\text{o}}}$, should be a linear function of the oxygen vacancy concentration and the activation energy is independent of the particular dopants. The experimental results for acceptor-doped oxides are inconsistent with these predictions [1–3]. The conductivity exhibits a maximum at the level of 12–20 m % of acceptor impurities, its activation energy increases with the concentration of dopants and depends upon their type [3].

Many authors have suggested that this behavior can generally be attributed to the interaction of defects in heavily acceptor-doped oxides [3–5]. Such suggestions are supported by the fact that at the acceptor content of 15%, the oxygen vacancies concentration reaches a value of 10^{21} cm^{-3} . They can not be considered as isolated centers and their interactions

are to be expected. The oxygen vacancies should experience two types of interactions; repulsion between themselves and other positively charged carriers and attraction with respect to the acceptor cations. The attractive interaction could result in the formation of dopant-vacancy complexes involving single vacancies bound to the isolated cations. This would result in the dopant being distributed between the complexes and isolated defects. Using Y_2O_3 -doped ZrO_2 as an example, essentially one half of the dopant will be associated with $(Y'_{\text{Zr}} - V_{\text{o}}^{\cdot\cdot})'$ complexes with the remainder being present as a Y'_{Zr} species. At higher concentration of dopants it is possible to create more complex associations which can form clusters. As a result of the high binding energy to these complexes, few oxygen vacancies will be available as free charges in the lattice. Experimental evidence in favor of the existence of these complexes has been given by Nowick who studied the dielectric and inelastic relaxation in Y_2O_3 -doped CeO_2 [4,6].

Additional support comes from the fact that the number of charge carriers which appears to be contributing to the electrical conductivity that is estimated from the lattice diffusion model is much less than that predicted from the acceptor concentrations and is also a highly non-linear function of that

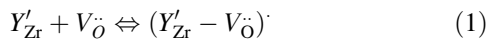
concentration as has been shown for SrCeO₃:5% Yb [7,8].

These observations strongly suggest that in the case of heavily acceptor-doped oxides, the use of the ionic conductivity model based on the assumptions of fully ionized and “free” oxygen vacancies is limited and questionable. As a result, models which address the electrical transport in these oxides must consider the interactions between the oxygen vacancies and the dopants.

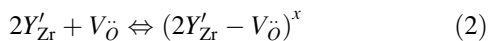
In the present work a model of electrical conductivity in solid electrolyte has been developed which will be able to describe the temperature and oxygen activity relationships between the ionic and electronic conductivity relative to the band structure and interaction between the defects and the lattice. In this model, dopant-oxygen vacancy and dopant-oxygen complexes which can create donor and acceptor levels are considered. The inclusion of complexes has made it possible to handle effects of defect interactions that were suspected of playing an important role in the motion of the ionic carriers. The proposed model correlates well with experimental data obtained for ZrO₂:16% Y and SrCeO₃:5% Yb oxygen conductors.

2. Defect Pair Model in Acceptor-Doped Oxides

The idea of defect pair formation in ionic conductors has been suggested by many authors and has been applied, for example to explain the temperature and P_{O_2} behavior of the electrical conductivity in acceptor-doped BaTiO₃ [5]. As an example, will be considered the defect pair formation in ZrO₂:Y. It is well established that the introduction of Y creates oxygen vacancies and acceptor centers. One half of dopants can form the acceptor-oxygen vacancy associations while the other will be present as Y'_{Zr} species [3,5].



For higher concentration of Y it is possible to form a neutral centers which will decrease the ionic conductivity due to reduction in the concentration of charge carriers:



Therefore, as the result of the defect pair formation, the introduction of the acceptor impurities creates

defects on both the cation and anion sublattices forming acceptor and donor centers. The possibility of forming such centers is supported by the binding energy calculation which shows for ZrO₂:Y the value of 0.35 and 0.7 eV for donor and neutral centers respectively. These values are in excellent agreement with the association energies determined experimentally [3,5]. Based on the reaction (1), the relation between the concentration of free oxygen vacancies and pair defects can be deduced. Assuming that the concentration of free oxygen vacancies is related to the equivalent positions in the cation sublattice [Zr] and the concentration of oxygen vacancies bounded into the complex $(Y'_{Zr} - V_{\ddot{O}})$ is proportional to the acceptors $[Y'_{Zr}]$, the ratio between the concentration of free vacancies and the concentration of pair defects can be estimated by the relation:

$$\frac{[V_{\ddot{O}}]}{[(Y'_{Zr} - V_{\ddot{O}})]} = \frac{[Zr]}{[Y'_{Zr}]} \cdot \exp\left(\frac{-E_{\text{assoc}}}{kT}\right) \quad (3)$$

where [Zr] is the concentration of cationic positions which for ZrO₂ is $1.5 \times 10^{22} \text{ cm}^{-3}$. Assuming the doping level to be 16% Y and the pair defect association energy (E_{assoc}) to be 0.35 eV, it is calculated that at 600°C the concentration of free oxygen vacancy will be one order of magnitude lower than that of the defect pairs. Using the association energy of 0.7 eV which is related to creation of more complex centers (2), when these are present, it appears that the concentration of free oxygen vacancies will be 3 orders of magnitude lower than that of the $(2Y'_{Zr} - V_{\ddot{O}})^x$ complexes. Based on these estimations, it appears that only a small fraction of the oxygen vacancies resulting from the dissociation of the donor centers will be free in the lattice which supports the hypothesis that in heavily acceptor-doped oxides, defect pair formation plays a predominant role.

From a formal point of view, Y-doped ZrO₂ can be considered as a compensated semiconductor with the acceptor (A) and donor (D) levels, which can be present in unionized (A^o , D^o) and ionized (A' , D') states. In both states we have the same type of defects but the differences are related to the localization of holes and electrons. Note that the acceptor described as A^o is a state attributed to the association of an electron hole and the defect generated when Y^{3+} is substituted for Zr^{4+} . In the case of the donor, D^o would represent the association of an electron and the

$(Y'_{Zr} - V_{\dot{o}})$ pair defect. This electron is related to the broken chemical bound between Zr^{4+} and O^{2-} ions as a result of oxygen vacancy introduction. The ionization of acceptor or donor states is attributed to dissociation of Y'_{Zr} and hole $-A^o \Leftrightarrow A' + h$ or $(Y'_{Zr} - V_{\dot{o}})$ and electron $- (D^o \Leftrightarrow D' + e$ respectively. It is important to point out that the donor ionization is not related to the change of Y^{3+} valence state.

The equilibrium between unionized donors and acceptors are related to the temperature and oxygen partial pressure by the relation:

$$\frac{[D^o]}{[A^o]} = rP_{O_2}^{-1/2} \quad (4)$$

where r is the equilibrium constant with standard exponential form $r = r_o \exp(-E/kT)$ related to the creation of oxygen vacancies. The relation between ionized (X^-) and unionized (X^o) acceptor or donor states can be determined using the Fermi equation [9,10]:

$$X^- = \frac{X^- + X^o}{1 + g \cdot \exp\left(\frac{E_x - F}{kT}\right)} \quad (5)$$

where X^- and X^o are the functions of the state densities for ionized and unionized levels, $E_x - F$ is the difference between the energy of the impurity and Fermi level and g is the factor connected with spin degeneration which for an electron equals 2. Substituting the acceptor ($[A^o]; [A']$) and donor ($[D^o]; [D']$) concentrations of unionized and ionized centers into Eq. (5) are obtained as:

$$[A^o] = \frac{1}{2}[A'] \cdot \exp\left(\frac{E_A - F}{kT}\right) \quad (6)$$

$$[D^o] = 2[D'] \cdot \exp\left(\frac{E_D - F}{kT}\right) \quad (7)$$

where E_A and E_D denotes the energy levels for acceptor and donor level respectively. Note that since the ionization of the donor center is connected with the dissociation of the $(Y'_{Zr} - V_{\dot{o}})$ complex, then the concentration of ionized donors should be related to the concentration of ionic carriers. The total concentration of impurity is related to the sum of ionized and unionized acceptors and donors:

$$[A^o] + [A'] + [D^o] + [D'] = [A] \quad (8)$$

Assuming that major charge carriers are related to

ionization of donors and acceptors, the electroneutrality equation will be:

$$[A'] = [D'] \quad (9)$$

From the Eqs. (4), (6), (7), and (9) the relationship between the Fermi energy, P_{O_2} and T becomes:

$$\exp\left(\frac{F}{kT}\right) = \left(rP_{O_2}^{-1/2}\right)^{1/2} \cdot \exp\left(\frac{E_D + E_A}{2kT}\right) \quad (10)$$

and finally the concentration of ionized donors and acceptors is:

$$[D] = [A'] = \frac{[A]}{2 + \frac{1}{2} \left[\left(rP_{O_2}^{-1/2}\right)^{-1/2} + \left(rP_{O_2}^{-1/2}\right)^{1/2} \right] \cdot \exp\left(\frac{E_A - E_D}{2kT}\right)} \quad (11)$$

As can be seen the concentration of ionized donors which is related to the concentration of ionic species depends upon the ambient atmosphere and the difference between the energy of the acceptor and donor levels, $\Delta E = E_D - E_A$. Based on this equation the dependence of the concentration of ionized donors as a function of P_{O_2} and ΔE can be calculated. The results of this calculation are presented in Fig. 1. As can be seen when $\Delta E > 1$ eV, the typical plateau for ionic species is observed. The value of this plateau, $\text{Log}(P'_{O_2}; /P''_{O_2})$ is very sensitive to ΔE and changes over the range of 2 to 40 when ΔE is varied from 0 to 2 eV respectively (insert Fig. 1, note that Log described Log_{10}). As ΔE increases, the preexponential factor in (11) tends to zero and the concentration of ionic species approaches $[A]/2$ which is the prediction for acceptor compensation by unassociated oxygen vacancies $[A'] = 2[V_{\dot{o}}]$; [3,5,10,11]. It should be pointed out that the region of oxygen partial pressure greater than 10 atm was not attainable and that due to high gas density Boltzman statistics do not apply above 10 atm. In this region the x -axis should be considered as oxygen activity rather than the pressure which has been marked in Fig. 1.

Equation (10) demonstrates that Fermi level in acceptor-doped oxides is a function of P_{O_2} and also depends upon the sum of $(E_D + E_A)/2$. The Fermi energy increases with decreasing P_{O_2} according to the relationship $F/kT \sim \text{Log } P_{O_2}^{-1/4}$ (Fig. 2). At low P_{O_2} , the Fermi level will be located between the donor and conduction band resulting in the generation of free electrons, while at high P_{O_2} , the presence of holes should be observed due to the Fermi level being located between the acceptor and valence band. For

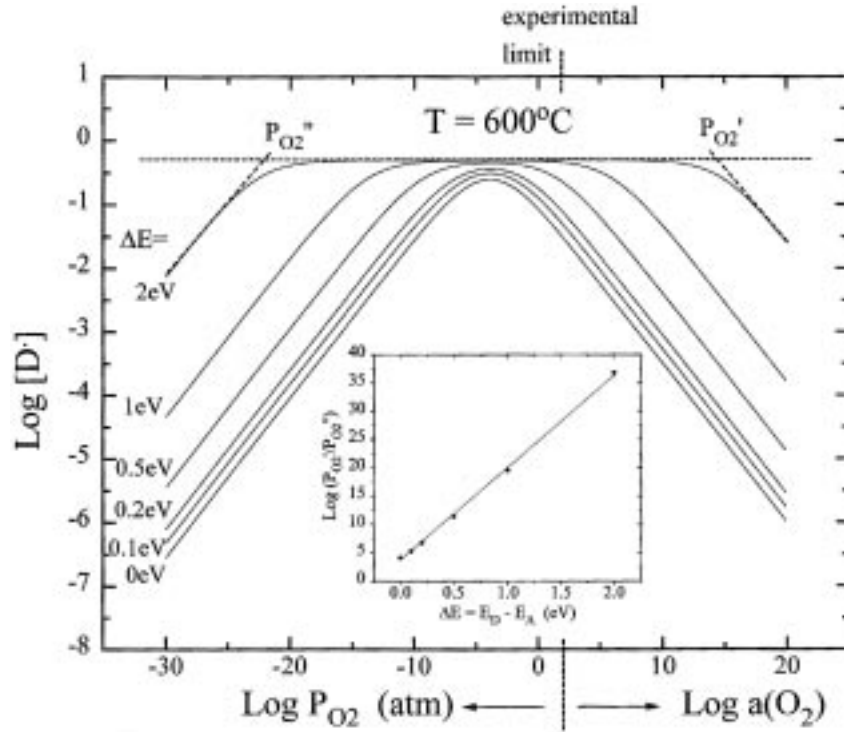


Fig. 1. Model prediction of the atmospheric dependence of the ionized donor concentration in acceptor-doped oxides for different $\Delta E = E_D - E_A$ (see Eq. 11). The insert is the dependence of $\text{Log}(P_{O_2}/P''_{O_2})$ which corresponds to P_{O_2} -independent ionized donor concentration as a function of ΔE .

this reason the model also should take into account the contribution of electronic (electrons and holes) species. The contribution of them we can describe by the Boltzman equations:

$$n = N_C \cdot \exp\left(\frac{F - E_C}{kT}\right) \quad (12)$$

$$p = N_V \cdot \exp\left(\frac{E_V - F}{kT}\right) \quad (13)$$

where N_C and N_V are the functions of state densities in conduction and valence bands respectively, E_C and E_V are the energy levels of those bands. After the substitution of the expression (10) into (12) and (13) are obtained:

$$n = N_C \cdot (rP_{O_2}^{-1/2})^{1/2} \exp\left(\frac{E_A + E_D - 2E_C}{kT}\right) \quad (14)$$

$$p = N_V \cdot (rP_{O_2}^{-1/2})^{-1/2} \exp\left(\frac{2E_V - E_A - E_D}{kT}\right) \quad (15)$$

As can be seen from Eqs. (14) and (15), the concentration of free electronic species follows the function of $P_{O_2}^{-1/4}$ and $P_{O_2}^{+1/4}$ for electrons and holes respectively which is in good agreement with experimental data and also with previously used models [11–13].

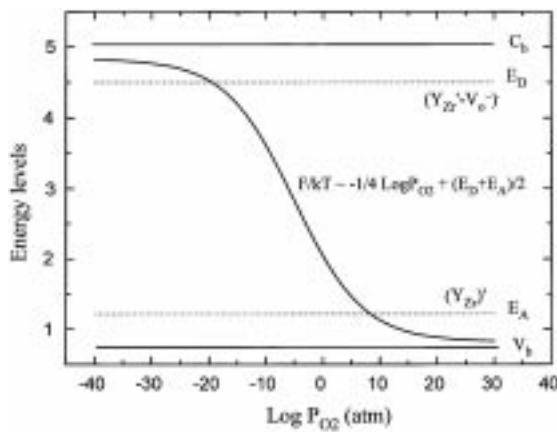


Fig. 2. The P_{O_2} dependence of Fermi level calculated for acceptor-doped oxides (see Eq. 10).

In summary it appears that the defect pair model successfully describes the temperature and oxygen partial pressure behavior for ionic (11) and electronic (14,15) species and predicts the P_{O_2} independent plateau for ionic and $P_{O_2}^{+1/4}$ behavior for electronic carriers respectively. In this model, the electrical conductivity is related to the oxide band structure and the localization of donor and acceptor levels. Based on this model the observed differences in activation energy of the conductivity and its nonlinear dependence upon the impurity concentration can be explained. The model suggests that ionic conductivity can occur by the jump of oxygen ions through the ionized defect associates as well as by the diffusion of the free oxygen vacancies. The model also explains the carrier concentration dependence upon P_{O_2} which is in good correlation with previous models. In addition the model is able to account for the charge compensation region where the ionic species concentration is independent with P_{O_2} and can change at very high and low oxygen pressure which has not been predicted by previous models.

Next predictions from the model are compared to the experimentally observed electrical conductivity behavior for $ZrO_2:16\%Y$ and $SrCeO_3:5\%Yb$ oxygen conductors.

3. Defect Pair Model Correlation with Experimental Data

Based on the model, expressions for the ionic and electronic conductivities in acceptor-doped oxides as a function of temperature and oxygen activity can be obtained. The use of Eqs. (11), (14) and (15) results in the expressions for the ionic, electronic and hole conductivities of the form:

$$\sigma_i = \frac{2[A]e\mu_i}{2 + \frac{1}{2} \left[\left(rP_{O_2}^{-1/2} \right)^{-1/2} + \left(rP_{O_2}^{-1/2} \right)^{1/2} \right] \cdot \exp\left(\frac{E_A - E_D}{2kT}\right)} \quad (16)$$

$$\sigma_e = e\mu_e N_C \left(rP_{O_2}^{-1/2} \right)^{1/2} \exp\left(\frac{E_A + E_D - 2E_C}{kT}\right) \quad (17)$$

$$\sigma_h = e\mu_h N_V \left(rP_{O_2}^{-1/2} \right)^{-1/2} \exp\left(\frac{2E_V - E_A - E_D}{kT}\right) \quad (18)$$

where μ_i , μ_e and μ_h are the mobility of ion, electron and hole carriers respectively. The region where the ionic conductivity exceeds the electronic conductivity

is defined by the oxygen pressures where $\sigma_i = \sigma_e$ and $\sigma_i = \sigma_h$. Since experimental data of the electrical conductivity for good ionic conductors ($ZrO_2:16\%Y$ and $SrCeO_3:5\%Yb$) is being compared, the energy levels for acceptors and donors are far apart so that $\Delta E = E_D - E_A > 2e$ which reduces the expression for ionic conductivity (16) to the form:

$$\sigma_i = [A]e\mu_i \quad (19)$$

Comparing the Eq. (17) with (19) and (18) with (19) results in the relations:

$$e[A]\mu_i = eN_C\mu_e \left(rP_{O_2}''^{-1/2} \right)^{1/2} \exp\left(\frac{E_A + E_D - 2E_C}{kT}\right) \quad (20)$$

$$e[A]\mu_i = eN_V\mu_h \left(rP_{O_2}'^{-1/2} \right)^{-1/2} \exp\left(\frac{2E_V - E_A - E_D}{kT}\right) \quad (21)$$

where P_{O_2}' and P_{O_2}'' denotes the high and low value of oxygen pressure corresponding to the ionic conductivity plateau. From the Eqs. (20) and (21) the expression for the ionic conductivity plateau becomes:

$$\frac{P_{O_2}'}{P_{O_2}''} = \left(\frac{[A]^2\mu_i^2}{N_V N_C \mu_h \mu_e} \right)^4 \exp\left(\frac{4E_g}{kT}\right) \quad (22)$$

where $E_g = E_C - E_V$ represents the energy gap. As can be seen from Eq. (21) the temperature dependence of the conductivity plateau is related to the band structure.

The band gap energy can be determined from the slope of relationship between the Log plateau of ionic conductivity and temperature:

$$\text{Log} \frac{P_{O_2}'}{P_{O_2}''} \sim 0.4343 \frac{4E_g}{T} \quad (23)$$

where $0.4343 = \text{Log}_{10}(e)$. This expression can be use for the examination the proposed pair defect model. As an example, the experimental data of the electrical conductivity of $ZrO_2:16\%Y$ and $SrCeO_3:5\%Yb$ are chosen. First both oxides are excellent ionic conductors with very broad P_{O_2} independent conductivity region [3,13]. The electronic and hole conductivities have been determined from nonsteady-state oxygen permeation measurements and have been found to be a few orders of magnitude lower than the ionic conductivity

[13]. The electrical conductivity behavior of $\text{SrCeO}_3:5\% \text{ Yb}$ confirms a hole and electron contribution at high and low P_{O_2} and a P_{O_2} -independent region at intermediate P_{O_2} related to the ionic conductivity [11]. The plateau of ionic conductivity has been found to be much higher for $\text{ZrO}_2:16\% \text{ Y}$ in comparison to that of $\text{SrCeO}_3:5\% \text{ Yb}$ which is in good correlation with the energy gap of 5 and 3.2 eV for these materials respectively [10,11]. This observation is also consistent with Eq. (23). Figure 3 represents the temperature behavior of $\text{Log}(P'_{\text{O}_2}/P''_{\text{O}_2})$ determined for $\text{ZrO}_2:16\% \text{ Y}$ based on the results of electrical conductivity measurements presented in [13]. As can be seen this yields an energy gap of 5.4 eV which is in excellent agreement with energy gap of 5.5 eV estimated as a sum of the electron and hole activation energy [13]. This energy gap also correlated well with the value of 5.62 eV recently reported for $\text{ZrO}_2:\text{Y}$ thin films [16]. Figure 4 is a similar plot of the ionic conductivity plateau data of $\text{SrCeO}_3:5\% \text{ Yb}$ [11] which indicates an energy gap of 3 eV (23) This value correlates well with optical measurements and theoretical calculations [14,15]. Based on the proposed model it appears that good ionic conductors should be characterized by wide energy gaps and also large difference in the energy between the acceptor and donor levels.

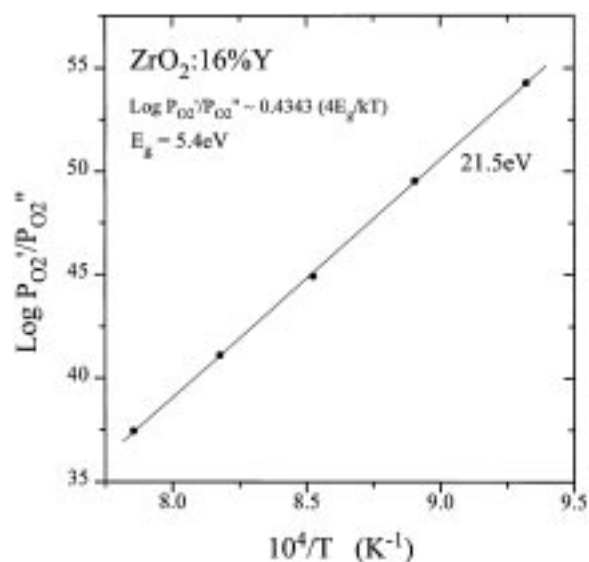


Fig. 3. The temperature dependence of $\text{Log}(P'_{\text{O}_2}/P''_{\text{O}_2})$ corresponding to P_{O_2} -independent electrical conductivity in $\text{ZrO}_2:16\% \text{ Y}$. Experimental data are from [13].

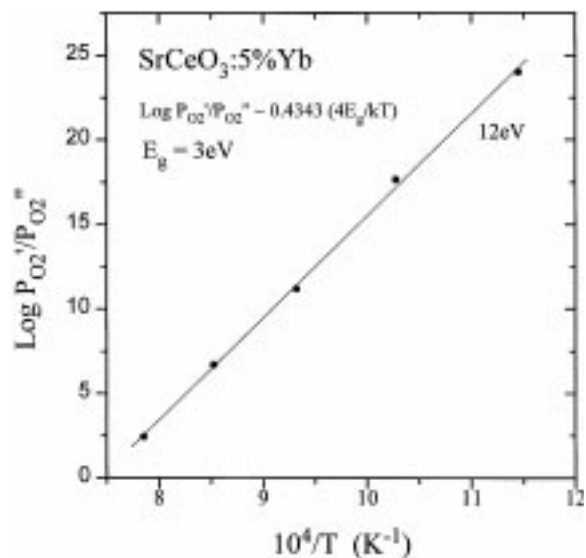


Fig. 4. The temperature dependence of $\text{Log}(P'_{\text{O}_2}/P''_{\text{O}_2})$ corresponding to P_{O_2} -independent electrical conductivity in $\text{SrCeO}_3:5\% \text{ Yb}$. Experimental data are from [11].

4. Conclusions

The model of the electrical conductivity in acceptor-doped oxides that has been developed by considering acceptor dopant-oxygen vacancy complexes which can create donor levels appears to correlate well with experimental data. The model suggests that due to the presence of these complexes, the concentration of free vacancies is much less than that of the complexes themselves with much of the ionic conductivity occurring by the jump of oxygen ions through the vacancies associated with ionized donors.

Correlation between the ionic conductivity and band structure has been obtained and has been found that it depends upon the energy differences between the donor and acceptor levels. If this difference is low, ionic conductivity can change as the function of $P_{\text{O}_2}^{+-1/4}$ at very high and low P_{O_2} which was not predicted in previous models. The transition from ionic to electronic conductivity is related to the movement of the Fermi level in the energy gap with oxygen partial pressure. It has been found that the electronic conductivity (electrons and holes) follows the function of $P_{\text{O}_2}^{+-1/4}$ which is in good agreement with previous theory and experiments.

The agreement between the model predictions and experimental data for oxygen conductors lends

support to the importance of defect complexes to their electrical conductivity behavior.

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