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COMMENT

Comment on Electrical Properties and Defect Structure of Barium Metatitanate within the *p*-Type Regime

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In a recent publication in this journal, Nowotny & Rekas discuss the defect chemistry of $BaTiO_3$ in the oxygen-excess, p-type regime.[1] They assert that the previously accepted model in which the major defects are acceptor impurities compensated by oxygen vacancies does not fit the experimental observations,[2-4] and they propose a new model based on cation vacancies. We believe that the problems they perceive with the extrinsic oxygen vacancy model (EOV) result from an incorrect comparison of the model with experimental results, and that the newly proposed cation vacancy (CV) model has serious inconsistencies. It is necessary to discuss these two models, denoted hereinafter as EOV and CV, in some detail in order to clarify the situation.

The Oxygen Pressure Dependence of the Equilibrium Conductivity

In the EOV model, except under extremely severe reducing conditions, the major defects are assumed to be acceptor impurities, either naturally occurring[2-4] or deliberately added,[5] and compensating oxygen vacancies. The condition of bulk charge neutrality is then dominated by the approximation

$$[A'] \approx 2[V_O^{\cdot\cdot}] \qquad (1)$$

where A' is a generalized single-level acceptor impurity such as Na'_{Ba} or Al'_{Ti}. The oxidation reaction is then taken to be the partial filling of these extrinsic oxygen vacancies from the atmosphere

$$V_O^{\cdot\cdot} + 1/2O_2 \rightleftharpoons O_O + 2h^{\cdot} \qquad (2)$$

with the mass-action expression

$$p^2/[V_O^{\cdot\cdot}] = K_p P(O_2)^{1/2} \qquad (3)$$

where $p = [h^{\cdot}]$. In the limit that eqn (1) is valid, p and the hole contribution to the conductivity are expected to vary as $P(O_2)^{1/4}$.

Nowotny & Rekas find fault with the EOV model because the observed equilibrium conductivity on the oxygen-excess side of stoichiometry does not always vary as $P(O_2)^{1/4}$. There are three separate reasons, all consistent with the EOV model, for the $P(O_2)$ dependence of the total conductivity to be less than $P(O_2)^{1/4}$:

(1) The contribution to the total conductivity by electrons: the electron and hole contributions are equal at the conductivity minima, and the electron contribution drops away gradually with increasing $P(O_2)$.

(2) The contribution to the total conductivity by oxygen vacancies: it has been shown that there is an ionic component to the total conductivity from the extrinsic oxygen vacancies.[4,6] Its effect is most noticeable near the minima, and its fractional contribution drops off with increasing $P(O_2)$ and temperature.

(3) The replacement of a significant fraction of the extrinsic oxygen vacancies by holes as a result of the oxidation reaction, eqn (2): this tends to flatten the $P(O_2)$ dependence of the total conductivity at high $P(O_2)$ and high temperature.

The first two factors tend to flatten the $P(O_2)$ dependence as the conductivity minima are approached from higher $P(O_2)$, while the third tends to

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flatten the $P(O_2)$ dependence at higher temperatures and $P(O_2)$. It is a simple exercise to show that with a tangential $P(O_2)$ dependence of the total conductivity of zero at the minima, and a tendency to approach a dependence of zero asymptotically as the vacancies are consumed with increasing $P(O_2)$, dependencies less than $P(O_2)^{1/4}$ can be expected in the region in between. With an electron contribution varying as $P(O_2)^{-1/4}$ and the level of ionic contribution previously determined,[4] it can be calculated that holes contribute 71%, 87% and 94% of the total conductivity at $P(O_2)$ values one, two and three orders of magnitude above that at the conductivity minima, respectively. In the high range of temperatures used by Nowotny & Rekas, 1268–1418 K, most of the remaining contribution is due to electrons. Their data extend about 3–1/2 orders of magnitude of $P(O_2)$ below 10^5 Pa (1 atm), and appear to extend about three to four orders above the minima, depending on the temperature. This is an insufficient range to observe conduction that is almost totally due to holes. It has been shown that for temperatures below about 1173 K, where the p-type region extends over a much wider range of $P(O_2)$, that the total conductivity varies precisely as $P(O_2)^{1/4}$ for $P(O_2)$ values more than 10^4 times that at the minima.[2,4] Moreover, it has been shown that the total conductivity over the $P(O_2)$ range above and below the minima are accurately represented by

$$\sigma_{\text{total}} = \sigma_{\text{ion}} + \sigma_n^0 P(O_2)^{-1/4} + \sigma_p^0 P(O_2)^{1/4} \quad (4)$$

where the latter two terms represent the contributions due to electrons and holes, respectively.

The apparent net acceptor content of the samples used in our earlier studies was about 60 ppm (based on formula units).[4,5] Using concentrations derived from the conductivities, half of the extrinsic oxygen vacancies will be filled by the oxidation reaction at 10^5 Pa (1 atm) at about 1330 K. Under these conditions, eqn (1) will no longer be an adequate approximation for charge neutrality, and the $P(O_2)$ dependence will begin to flatten significantly at high $P(O_2)$. This temperature is toward the lower end of the range used by Nowotny & Rekas.

Nowotny & Rekas use the following approximation for charge neutrality for the p-type region

$$[A'] \approx 2[V_O^{\cdot\cdot}] + p \quad (5)$$

It is increasingly important to include holes in this expression as the vacancies become significantly consumed, as described above. These authors express the vacancy concentration in eqn (5) in terms of the hole concentration and $P(O_2)$, using the appropriate mass-action expressions. The result was rearranged into a linear equation between the conductivity and $P(O_2)$. The failure of their data to fit this linear function was taken as an indication of failure of the EOV model. This treatment considers only hole conduction, and, as shown above, contributions from electrons, and even ions, cannot be neglected for $P(O_2)$ values near the conductivity minima. Indeed, the failure to fit the linear function increases with decreasing $P(O_2)$ as the electron contribution becomes increasingly important. The data of Nowotny & Rekas do not cover a range where the linear expression would be a valid test of the EOV model. Moreover, the derived expression fails completely when eqn (1), the essence of the EOV model, is valid, because the hole concentration then vanishes as the difference between two equal terms.

Nowotny & Rekas also point to a slight temperature dependence of the apparent net acceptor content, as derived from a fit of the EOV model to experimental results,[4,5] as a deficiency in that model. The variation is very modest, amounting to a decrease in the apparent concentration by about 30% from 1000 to 750°C, and could have resulted from a variety of minor uncertainties, such as the exact temperature dependence of the electron mobility. In fact, if a mobility dependence of T^{-1}, as suggested by Seuter in interpreting his Hall effect data,[7] had been used instead of $T^{-3/2}$, as used by us, the derived acceptor content would have been even less dependent on the temperature. This is not an adequate basis for discarding a model that fits the major features extremely well.

The Proposed CV Model

The essence of this model is that the oxidation reaction involves the creation of cation vacancies

$$3/2O_2 \rightleftharpoons 3O_O + V_{Ba}'' + V_{Ti}^{4'} + 6h^{\cdot} \quad (6)$$

with its mass-action expression

$$[V_{Ba}''][V_{Ti}^{4'}]p^6 = K_2 P(O_2)^{3/2} \quad (7)$$

and that the oxygen vacancy concentration is negligible. It can be immediately seen that the only way to obtain the proportionality of the hole concentration to $P(O_2)^{1/4}$ is for the cation vacancy concentrations to be independent of $P(O_2)$. This is not possible in the CV model, in which it is proposed that ionic defects result only from the same oxidation reaction that creates the holes.

The enthalpies of oxidation and reduction have been determined to be 0·92 and 5·90 eV per added or subtracted oxygen, respectively.[4] If eqn (6) is algebraically added to three times eqn (2), the result is

$$\mathrm{nil} \rightleftharpoons V''_{\mathrm{Ba}} + V^{4'}_{\mathrm{Ti}} + 3V^{\cdot\cdot}_{\mathrm{O}} + 6\mathrm{e}' + 6h^{\cdot} \qquad (8)$$

whose total enthalpy should then be

$$3(5{\cdot}90 + 0{\cdot}92)\,\mathrm{eV} = 20{\cdot}46\,\mathrm{eV}$$

Equation (8) is also the sum of the formation of intrinsic Schottky disorder and six times the band gap. The latter, as determined by an Arrhenius plot of the conductivities at the minima, is 3·27 eV.[4] Six times 3·27 eV is 19·63 eV, which leaves only 0·83 eV for the enthalpy of formation of a mole of Schottky defects. That is only about one third of the enthalpy for the formation of Schottky disorder in NaCl,[8] which involves only two singly charged vacancies. The enthalpic residue is actually even less because the conductivity minima contain a small contribution from ionic conduction that has a smaller temperature dependence, thus the true band gap is slightly larger than 3·27 eV.[4,5] In any case the discrepancy is enormous; theoretical calculations by Lewis & Catlow indicate that the enthalpy of formation of a mole of Schottky defects in $BaTiO_3$ is of the order of 11–12 eV.[9] The lack of any thermal activation for the concentrations of the dominant defects in the near-stoichiometric region is in accord with the EOV model, where these defects are acceptor impurities and their compensating oxygen vacancies.

Nowotny & Rekas agree that oxygen vacancies are the major ionic defect in oxygen-deficient compositions. However, they assume that 'the concentration of oxygen vacancies within the *p*-type regime is negligibly low'. It is not possible to account for such an abrupt switch in defect types by conventional defect chemistry. Moreover, the presence of different defects on opposite sides of the stoichiometric composition cannot be reconciled with the observation of a $P(O_2)$-independent ionic contribution to the conductivity that is the same on both sides.[6]

One of the attractive features of the EOV model is that it explains why the enthalpy of oxidation, 0·92 eV per oxygen, is so much smaller than the enthalpy of reduction, 5·90 eV per oxygen. According to eqn (2), the oxidation reaction in this model, lattice defects are actually consumed by oxidation, and the accommodation of the extra oxygen is by the very favorable process of filling vacant oxygen sites. It is extremely unlikely that oxidation with the formation of barium and titanium vacancies would involve such a small enthalpy.

Conclusions

It is shown that the generally accepted extrinsic oxygen vacancy model for the defect chemistry of undoped and acceptor-doped $BaTiO_3$ is in good agreement with the experimental observations when the model is correctly applied. The lack of agreement found by Nowotny & Rekas resulted from neglect of the contributions of electrons and oxygen vacancies to the total conductivity, and of the significant replacement of vacancies by holes from the oxidation reaction. The alternative cation vacancy model proposed by these authors is in serious disagreement with a number of experimental observations and is internally inconsistent.

A useful test for the self-consistency of a defect model is to see if it can be represented by a sensible Kroger–Vink diagram. The proposed cation vacancy model for $BaTiO_3$ fails that test.

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