*Journal of the European Ceramic Society* 9 (1992) 467–470

## RESPONSE

# *Reply:* On the Defect Structure of $BaTiO_3$

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## I Introduction

In his comments Smyth[1] claims that the Schottky disorder considered for $BaTiO_3$ in our work[2] is based on incorrect fit of the model with experimental data. Smyth has compared the extrinsic and intrinsic models, denoted by him as EOV and CV, respectively, in order to decide which of the two models is valid and which is wrong. He argues that the extrinsic model is the correct one because his data are in excellent agreement with this model. According to Smyth a fit, if correct, should always result in a confirmation of the extrinsic model. He claims that the intrinsic model is internally inconsistent.

Our basic answer to the comments of Smyth[1] is that only the model which is based on a general lattice electroneutrality condition may be considered as valid without limitations.[3] Other models, which are based on simplified lattice electroneutrality conditions such as the extrinsic model, have limited validity. It will be shown that this model is unacceptable in the *p*-type regime.

## II General Defect Model

It has been well documented that both cation and oxygen sublattices of $BaTiO_3$ are defected. Therefore, assuming that all defects are fully ionized the charge neutrality condition for pure $BaTiO_3$ requires that

$$[h^{\bullet}] + 2[V_{\mathrm{O}}^{\bullet\bullet}] = 2[V_{\mathrm{Ba}}''] + 4[V_{\mathrm{Ti}}''''] + [\mathrm{e}'] \qquad (1)$$

In the presence of impurities condition (1) takes the following form:

$$[h^{\bullet}] + 2[V_{\mathrm{O}}^{\bullet\bullet}] + [D^{\bullet}] = 2[V_{\mathrm{Ba}}''] + 4[V_{\mathrm{Ti}}''''] + [A'] + [\mathrm{e}'] \qquad (2)$$

where $D^{\bullet}$ and $A'$ denote donor and acceptor impurities, respectively.

Since the model based on eqn (2) is mathematically intractable several other models, based on simplified charge neutrality conditions, have been proposed. One should realize, however, that whatever approximation is made it will result in an error caused by ignoring certain defects which might be the minor ones but still may not be negligible. Therefore, in considering models based on simplified charge neutrality conditions there is always a dilemma: which defects can be assumed as predominant and which can be ignored?

## III The Extrinsic Model

Long & Blumenthal[4] have proposed an extrinsic model which has been later used by Smyth *et al.* to interpret their data.[1,5–7] This model assumes that acceptor-type impurities are the predominant defects. Assuming also that the concentration of both

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*Journal of the European Ceramic Society* 0955-2219/92/$05.00 © 1992 Elsevier Science Publishers Ltd, England. Printed in Great Britain

electron carriers ie negligible, eqn (2) takes the form

$$2[V_O^{\bullet\bullet}] = [A']^* \qquad (3)$$

where $[A']^*$ is the effective concentration of acceptors defined as the difference between the concentration of acceptors (multiplied by their effective charge) and the concentration of donors (multiplied by their effective charge):

$$[A']^* = [A'] - [D^{\bullet}] \qquad (4)$$

Then, for the $n$- and $p$-type regions, we have, respectively,

$$[e'] = K_n^{1/2}(2/[A']^*)^{1/2} p(O_2)^{-1/4} \qquad (5)$$

$$[h^{\bullet}] = K_i K_n^{-1/2}(1/2[A']^*)^{-1/2} p(O_2)^{1/4} \qquad (6)$$

where $K_i$ and $K_n$ are equilibrium constants of the respective reactions:

$$\mathrm{nil} \rightleftharpoons e' + h^{\bullet} \qquad (7)$$

$$O_O \rightleftharpoons 1/2O_2 + V_O^{\bullet\bullet} + 2e' \qquad (8)$$

Smyth[1] claims that the extrinsic model results in an excellent fit with experimental data and assumes this model to have a general validity regardless of nonstoichiometry and impurity content.

One may expect that oxygen vacancies are the predominant defects at lower $p(O_2)$, i.e. in the $n$-type regime. Therefore, the extrinsic model may be recommended for very contaminated specimens within the $n$-type regime. It is clear, however, that the concentration of oxygen vacancies will decrease with increase of $p(O_2)$ and, at the same time, the concentration of cation vacancies will assume substantial values which cannot be ignored.[8,9] Therefore, the extrinsic model will not be valid for relatively pure specimens at oxidizing conditions (the $p$-type regime).

One should emphasize here that the $p(O_2)$ exponent takes the values $-1/4$ and $1/4$ (for $n$- and $p$-type regime, respectively) not only for the extrinsic model but also for several other models, such as the nonstoichiometric model reported by Seuter.[10] Accordingly, a conclusion that the extrinsic model is confirmed as valid just because the $p(O_2)$ exponent assumes $-1/4$ or $1/4$ is incorrect.

## IV The Intrinsic Model

In our recent study[2] we have considered experimental data of both $\sigma$ and thermopower ($\alpha$) within the $p$-type regime in terms of both the extrinsic and the intrinsic models.

The intrinsic model is based on the Schottky disorder:[11,12]

$$\mathrm{nil} \rightleftharpoons 3V_O^{\bullet\bullet} + V_{Ba}'' + V_{Ti}'''' \qquad (9)$$

Assuming that the effective concentration of acceptor-type impurities is negligible the general charge neutrality eqn (2) takes the form of (1). Assuming also that the cation sublattice is stoichiometric (Ba/Ti = 1) eqn (1) may be considered within three regimes:

(1) *High temperature and low* $p(O_2)$. This regime is termed by Smyth[1] as corresponding to the 'severe reducing conditions'. Then concentrations of cation vacancies and electron holes assume negligible values. Consequently

$$2[V_O^{\bullet\bullet}] = [e'] \qquad (10)$$

Applying the mass action law to equilibrium (8), we can write

$$[e'] = (2K_n)^{1/3} p(O_2)^{-1/6} \qquad (11)$$

(2) *Intermediate regime.* This regime corresponds to $p(O_2)$ around the $n$–$p$ transition. Then all intrinsic defects assume comparable values:

$$[V_O^{\bullet\bullet}] = [V_{Ba}''] + 2[V_{Ti}''''] \qquad (12)$$

Applying the mass action law to eqns (1) and (8), we have

$$[e'] = K_n^{1/2}(9K_s)^{-1/10} p(O_2)^{-1/4} \qquad (13)$$

$$[h^{\bullet}] = K_i K_n^{-1/2}(9K_s)^{1/10} p(O_2)^{1/4} \qquad (14)$$

and

$$[V_O^{\bullet\bullet}] = (9K_s)^{1/5} \qquad (15)$$

where $K_s$ denotes equilibrium constant of the Schottky disorder.[1]

The above relationships indicate that the Schottky disorder (9) results in the same $p(O_2)$ exponent as the extrinsic model. In other words, *the value of the* $p(O_2)$ *exponent cannot serve as an argument in comparing the validity of the two models.* Moreover, taking into account that the mobility of oxygen vacancies is much higher than that of cation vacancies,[13,14] at comparable concentrations (see eqn (12)) the ionic conductivity component will mainly correspond to the mobility of oxygen vacancies. Accordingly, *an analysis of the ionic conductivity component cannot serve to distinguish between the two models.*

(3) *High temperatures and high* $p(O_2)$. This regime can be termed as corresponding to

'severe oxidizing conditions'. Then the concentration of electron holes may assume high values which cannot be ignored. Accordingly

$$[h^{\cdot}] = 2[V''_{\mathrm{Ba}}] + 4[V''''_{\mathrm{Ti}}] \qquad (16)$$

Applying the mass action law to equilibria (8) and (9), we have

$$[h^{\cdot}] = (36K_i^6 K_s K_n^{-3})^{1/8} p(\mathrm{O}_2)^{1/5{\cdot}33} \qquad (17)$$

Equation (17) enables one to explain $p(\mathrm{O}_2)$ exponent values which are lower than 1/4, such as 1/5·33.

## V Effect of Electron and Ionic Contributions on the *p*-Type Conduction

Smyth[1] has discussed the effect of the electron and ionic contributions to conduction within the *p*-type regime. According to Smyth[1] the electron and ionic contributions are responsible for an apparent decrease of the exponent from 1/4 (predicted by the extrinsic model for pure hole conduction) to much lower values which we have interpreted in terms of the intrinsic model.[2] In other words, Smyth claims that the slope determined by us includes both the hole conduction component, which is exactly 1/4, and the electron and ionic conduction components. Let us confront the conclusions of Smyth[1] with literature reports on properties of BaTiO$_3$.

Based on the electron mobility data reported by Seuter[10] and assuming (after Chan *et al.*[7]) that the mobility of electrons is twice that of holes the electron and ionic contributions may be determined. For calculation of the equilibrium constant $K_i$ we have taken experimental data of $\sigma$ values corresponding to extremely reducing conditions, corresponding to the $p(\mathrm{O}_2)$ slope equal to $-1/6$. Based on relationship (18) proposed by Smyth *et al.*,[1,15] we have determined both $\sigma_n$ and $\sigma_p$ components. Then the equilibrium constant $K_i = [h^{\cdot}][\mathrm{e}']$ was evaluated. Assuming that $\sigma_{\mathrm{ion}}$ is independent of $p(\mathrm{O}_2)$ we have

$$\sigma_{\mathrm{tot}} = \sigma_{\mathrm{ion}} + \sigma_n^0 p(\mathrm{O}_2)^{-1/4} + \sigma_p^0 p(\mathrm{O}_2)^{1/4} \qquad (18)$$

$$\begin{aligned} 1/n_{\mathrm{extr}} &= [\partial \ln \sigma_{\mathrm{tot}}/\partial \ln p(\mathrm{O}_2)] \\ &= (\sigma_n/\sigma_{\mathrm{tot}})[\partial \ln \sigma_n/\partial \ln p(\mathrm{O}_2)] \\ &\quad + (\sigma_p/\sigma_{\mathrm{tot}})[\partial \ln \sigma_n/\partial \ln p(\mathrm{O}_2)] \\ &= 1/n_n(\sigma_n + \sigma_{\mathrm{tot}}) + 1/n_p(\sigma_p/\sigma_{\mathrm{tot}}) \qquad (19) \end{aligned}$$

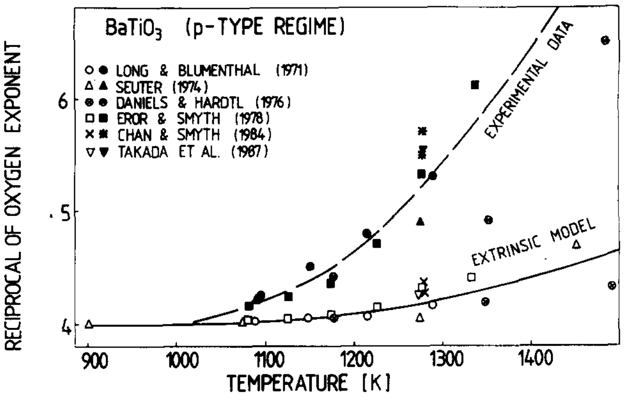

**Fig. 1.** Reciprocal of the oxygen exponent determined experimentally ($n_{\mathrm{exp}}$—heavy points)[4,6,8,16–18] and that determined by using the extrinsic model ($n_{\mathrm{extr}}$—empty points) for undoped BaTiO$_3$ in the *p*-type regime.

where $n_n$ and $n_p$ denote reciprocals of the $p(\mathrm{O}_2)$ exponent values corresponding to the electron and electron hole components, respectively, and $n_{\mathrm{extr}}$ is the value determined according to extrinsic model (eqn (19)). Assuming (after Smyth[1]) that $1/n_n$ and $1/n_p$ are equal to $-1/4$ and $1/4$ for the *n*- and *p*-type regimes, respectively, we have determined the parameter $n_{\mathrm{extr}}$. Figure 1 illustrates both majority of experimental data of the reciprocal of the oxygen exponent for undoped BaTiO$_3$ ($n_{\mathrm{exp}}$),[4,6,8,16–18] including data reported by Smyth *et al.*,[6,16] and $n_{\mathrm{extr}}$ which is predicted by the extrinsic model. As seen the electron and ionic components assume negligible values in the *p*-type regime up to 900–1050 K. The electron and ionic components result in the increase of $n_{\mathrm{extr}}$ to about 4·20 at 1300 K and about 4·8 at 1400 K. As clearly seen from Fig. 1, however, the parameter $n_{\mathrm{exp}}$ assumes much higher values than those predicted by the extrinsic model.

It seems that any model considered for the *p*-type regime cannot ignore the formation of intrinsic defects such as Ba and Ti vacancies. Speculations concerning the enthalpy balance, which discard the intrinsic model, have been based on values determined by using theoretical methods. However, as it has been shown by Tetot & Gerdanian,[19] the enthalpy values determined by theoretical methods may differ by orders of magnitude from experimental ones. Therefore, any discussion on the enthalpy balance of defect reactions should be based on experimental data.

## Conclusions

We have shown that the validity of the extrinsic model is limited to a narrow range of the *n*-type regime. This model is in conflict with experimental data reported for BaTiO$_3$ in the *p*-type regime. Accordingly, the basic conclusion of Smyth[1] concerning the applicability of the extrinsic model in this regime is unacceptable.

## Acknowledgements

Support of the Commonwealth of Australia through the Department of Industry, Technology and Commerce (Grant #C91/02826) as well as the Commission of the European Communities (Grant #BREU-0144-C) is gratefully acknowledged.

Thanks are due to C. Ball and A. Hilton for their comments.

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