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Oxygen activity dependence of the defect structure of La-doped $BaTiO_3$

M. M. NASRALLAH*, H. U. ANDERSON, A. K. AGARWAL,
B. F. FLANDERMEYER
Department of Ceramic Engineering, University of Missouri-Rolla, Rolla, Missouri 65401, USA

A model for the behaviour of donor-doped $BaTiO_3$ as a function of oxygen activity is proposed. Thermogravimetric measurements show good agreement with the proposed model. The results show that donor-doped $BaTiO_3$ is stoichiometric with electronic compensation of the donor at low oxygen activity, but with increasing oxygen activity, compensation becomes ionic as excess oxygen is absorbed. The possible compensation mechanisms are discussed.

1. Introduction

Several studies [1–10] have shown that at high temperature $BaTiO_3$ exhibits n-type behaviour due to oxygen deficiency. This behaviour is extended over a wide range of partial oxygen pressures within the low P_{O_2} region. At higher oxygen activities, generally p-type behaviour predominates due to acceptor-type defects. The defect structure in these two characteristic regions has a clear impact on the room temperature electrical properties of $BaTiO_3$. Equilibration in reducing atmospheres [11] results in a dark-coloured n-type semiconductor, whereas equilibration in oxidizing atmospheres [12] produces a light-coloured p-type insulator, provided that the samples are quenched from high temperature to room temperature. In reduced $BaTiO_3$ conduction is attributed to a band-type mechanism [13–15], rather than to the hopping process, due to the presence of the so called F-centres related to electrons trapped at oxygen vacancy sites in the vicinity of two Ti^{4+} and four Ba^{2+} ions.

The role of impurities on the defect structure of $BaTiO_3$ has been recently emphasized by Chan *et al.* [10], who concluded that with currently available purities a net excess of acceptor-type defects exists in amounts exceeding the concentrations of intrinsic ionic or electronic disorders in $BaTiO_3$. Intentional dopants of higher valent ions at Ba^{2+} or Ti^{4+} sites introduce additional donor levels, thus increasing the n-type conductivity, whereas lower valent ions favour p-type conduction. It is therefore expected that additions of Gd^{3+} or La^{3+} on Ba^{2+} sites and Nb^{5+} or Sb^{5+} on Ti^{4+} sites favour n-type behaviour whereas, Mg^{2+}, Ga^{3+}, Fe^{3+} or Al^{3+} on Ti^{4+} sites will enhance p-type behaviour. Generally, selective substitution on either Ba^{2+} or Ti^{4+} sites is feasible because of the large difference in their respective ionic radii, thus allowing the well-known ferroelectric compound $BaTiO_3$ to be transformed into a conductor by utilizing Verwey's controlled valency model [16].

Acceptor dopants seem to have a relatively small effect on the conductivity of $BaTiO_3$ because of their large ionization energy [17] (2.2 eV), however, they can act as traps. For example, upon cooling gallium-doped $BaTiO_3$ from 1300° C to room temperature, the concentration of electrons can be reduced appreciably by the acceptor dopant so that even specimens prepared in reducing atmosphere remain insulators. The effect of Al^{3+} appears to be an extension [18] of the behaviour of undoped $BaTiO_3$, in which an accidental net excess of acceptors, already present, play an important role. Aluminium was found to be at best 30% effective in creating new acceptor levels. However, acceptor doping with several iron group elements up to the solubility limit of 2 mol % has

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*On leave from the Faculty of Engineering, Cairo University, Egypt.

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been investigated [19] and the results interpreted in terms of oxygen vacancy compensation for valence changes of the 3*d* dopant. The sites occupied by Gd^{3+} depend on the Ba:Ti ratio [14, 20], with the amount of Gd^{3+} at Ba^{2+} sites decreasing as the Ba:Ti ratio increases from 0.994 to 1.015. For La^{3+}-doped $BaTiO_3$, it is generally accepted that La^{3+} occupies the Ba^{2+} site and the excess charge may be compensated either by electrons which are assumed present in the titanium 3*d* conduction band or by barium and/or titanium site vacancies, although a small polaron hopping model [21] has been proposed for minor additions of lanthanum. Shirasaki *et al.* [22] suggest the presence of barium and titanium vacancies in lanthanum-doped $BaTiO_3$. Jonker *et al.* [23] favour titanium vacancy compensation for the donor dopant at lower temperatures, whereas at higher temperature, under reducing conditions, the excess charge is compensated by Ti^{3+} ions. It has been further claimed [14] that some of the La^{3+} dopant may substitute Ti^{4+} ions and act as acceptors. This was found to be dependent on the Ba:Ti ratio. It is therefore obvious that several models and discrepancies exist for the behaviour of lanthanum-doped $BaTiO_3$. In this study a defect structure model is proposed and verified by analysis of thermogravimetric (TGA) data on lanthanum-doped $BaTiO_3$ as a function of temperature and oxygen activity.

2. Proposed model

It has been shown that TiO_2 is practically insoluble in $BaTiO_3$ [24]. Therefore, instead of assuming that a Schottky-type defect reaction prevails in this system, the assumption is made that excess TiO_2 is in equilibrium with the oxide as an external phase. Using Kröger–Vink notation [25], the reaction for the incorporation of excess TiO_2 into $BaTiO_3$ can be written as follows:

$$TiO_2 \rightleftarrows Ti_{Ti} + 2O_O + V''_{Ba} + V_O^{\cdot\cdot} \qquad (1)$$

Assuming dilute solution, the mass action expression for Equation 1 is

$$[V''_{Ba}][V_O^{\cdot\cdot}] = K_1 A_{TiO_2} \qquad (2)$$

where A_{TiO_2} is the activity of TiO_2. Equation 2 will prevail over a wide P_{O_2} range and will become negligible only at both extremes of the oxygen activity range. If this is considered a closed system, the concentration of V''_{Ba} cannot change without exsolving a second phase. Thus, $[V''_{Ba}] = (K_1 A_{TiO_2})/[V_O^{\cdot\cdot}]$ = constant throughout the single phase region of $BaTiO_3$.

The reaction by which $BaTiO_3$ becomes non-stoichiometric by the loss of oxygen can be written as follows:

$$O_O \rightleftarrows V_O^{\cdot\cdot} + 2e + \tfrac{1}{2}O_2 \qquad (3)$$

(fully ionized defects are assumed throughout). The equilibrium constant for this reaction is

$$K_3 = [V_O^{\cdot\cdot}]n^2 P_{O_2}^{1/2} \qquad (4)$$

The donor impurity (La^{3+}) is assumed to substitute Ba^{2+} on normal lattice sites, thus additional charge carriers are introduced into the system. This requires the following neutrality condition:

$$2[V''_{Ba}] + n = 2[V_O^{\cdot\cdot}] = [La_{Ba}^{\cdot}] \qquad (5)$$

The dominant defects are dependent on the oxygen activity, temperature and concentration of dopant. The following cases are considered:

1. $[La_{Ba}^{\cdot}]$ and non-stoichiometry small.

$$[V''_{Ba}] = [V_O^{\cdot\cdot}] = \text{constant}$$

It follows, from Equation 4, that the electron concentration becomes,

$$n = \left(\frac{K_3}{[V_O^{\cdot\cdot}]}\right)^{1/2} P_{O_2}^{-1/4} \qquad (6)$$

2. $[La_{Ba}^{\cdot}]$ is small and non-stoichiometry large. The neutrality condition is then,

$$n = 2[V_O^{\cdot\cdot}]$$

and the oxygen vacancy concentration becomes,

$$[V_O^{\cdot\cdot}] = \left(\frac{K_3}{4}\right)^{1/3} P_{O_2}^{-1/6} \qquad (7)$$

3. $[La_{Ba}^{\cdot}]$ is large.

The neutrality condition is given by

$$n = [La_{Ba}^{\cdot}] \begin{array}{l} \gg [V''_{Ba}] \\ \gg [V_O^{\cdot\cdot}] \end{array}$$

which yields from Equations 2 and 4

$$[V''_{Ba}] = \frac{K_1}{[V_O^{\cdot\cdot}]} A_{TiO_2} = \text{constant},$$

and

$$[V_O^{\cdot\cdot}] = \frac{K_3}{[La_{Ba}^{\cdot}]^2} P_{O_2}^{-1/2} \qquad (8)$$

Under reducing conditions, the donor is compensated electronically by formation of Ti^{3+}, whereas at high P_{O_2}, stoichiometric excess oxygen is added to the system, resulting in formation of barium-rich phases and V''_{Ba} in the host lattice, thus the carrier concentration is given by

$$n = [La^{\bullet}_{Ba}] - 2[V''_{Ba}]$$

If one considers a structural accommodation in an ordered fashion whereby layers of BaO of the Ruddlesdon–Popper [26] type are formed (other possible barium-rich phases, similar to those suggested by Tilley [27] for the $SrTiO_3$ system, will not affect the validity of the model), the defect reaction is accordingly given by:

$$Ba_{1-y-x}La^{\bullet}_{y}V''_{Ba_x}Ti'_{y-2x}Ti_{1-y+2x}O_3 + xBaO \underset{\text{oxid.}}{\overset{\text{red}}{\rightleftarrows}}$$

$$Ba_{1-y}La^{\bullet}_{y}Ti'_{y}Ti_{1-y}O_3 + \frac{x}{2}O_2 \qquad (9)$$

where y = moles lanthanum, and x = moles oxygen.

This reaction can be reduced to:

$$BaO + 2Ti + V''_{Ba} \underset{\text{oxid.}}{\overset{\text{red}}{\rightleftarrows}} Ba + 2Ti' + \tfrac{1}{2}O_2 \qquad (10)$$

Assuming that the activities can be approximated by the corresponding mole fraction, the equilibrium constant is given by:

$$K_{10} = \frac{[Ba][Ti']^2}{[BaO][Ti]^2[V''_{Ba}]}P_{O_2}^{1/2}$$

$$= \frac{(1-y-x)(y-2x)^2}{x^2(1-y+2x)^2}P_{O_2}^{1/2} \qquad (11)$$

For computational purposes, Equation 11 can be rearranged to yield an expression for the excess oxygen x,

$$x = \frac{2yP_{O_2}^{1/4}}{(2-y)K_{10}^{1/2} + 4P_{O_2}^{1/4}} \qquad (12)$$

The electrical conductivity $\sigma = e\mu n$, where the carrier concentration $n = y - 2x$, is given by substitution in Equation 12,

$$\sigma = \frac{e\mu y(2-y)K_{10}^{1/2}}{(2-y)K_{10}^{1/2} + 4P_{O_2}^{1/4}} \qquad (13)$$

At low P_{O_2} (electronic compensation) $n = y$, thus $\sigma = e\mu y$ and

$$x = \frac{2y}{(2-y)K_{10}^{1/2}}P_{O_2}^{1/4} \qquad (14)$$

At high P_{O_2}, (V''_{Ba} compensation), $x = y/2$ and,

$$\sigma = \frac{e\mu y(2-y)K_{10}^{1/2}P_{O_2}^{-1/4}}{4} \qquad (15)$$

Accordingly, as a result of donor doping, the model predicts that the compensation changes from electrons at low P_{O_2} and/or high donor concentration to cation vacancies at high P_{O_2}. A schematic representation of the model can be obtained from plots showing predominant defects at various oxygen activities. Such plots can be experimentally verified by weight change and conductivity measurements as a function of oxygen activity and temperature. In a recent publication [28] the authors illustrated the importance of these diagrams and the regions where the compensation changes for both p-type and n-type oxides. Analysis of thermogravimetric data and its correlation to the model is the subject of this publication.

3. Experimental details

A series of lanthanum-doped $BaTiO_3$ compositions were prepared by the liquid mix process [29]. In all cases stoichiometric A/B ratio was maintained, i.e. $(Ba + La)/Ti = 1$, as the lanthanum content ranged from 0 to 15 at %.

Thermogravimetric measurements were conducted in a system designed to detect weight changes on a 50 to 80 g sample to an accuracy of ± 1 mg ($\sim 10^{-5}$ moles) at 1200 to 1400° C in an atmosphere of 10^{-11} to 10^{5} Pa oxygen. The oxygen activity was maintained by flowing gas mixtures of either N_2O_2 or $CO_2/H_2/N_2$. A calibrated ZrO_2 oxygen sensor was used to monitor the oxygen partial pressure. The details of the apparatus are given elsewhere [30].

4. Results and discussion

Reaction 9 predicts that lanthanum-doped $BaTiO_3$ can gain excess oxygen beyond the stoichiometric level through the formation of a second phase, with the maximum amount of excess oxygen given by $O_{xs} = \frac{1}{2}[La^{\bullet}_{Ba}]$. Fig. 1 is a plot showing the oxygen exchange as a function of P_{O_2} for 4 at % lanthanum-doped $BaTiO_3$ at 1247 to 1400° C. Within this temperature range, stoichiometric oxygen compositions are found only in the low oxygen activity region $\sim 10^{-5}$ Pa, whereas at higher P_{O_2}, stoichiometric excess of oxygen is incorporated into the $BaTiO_3$ lattice, with the accompanying formation of cationic defects. These defects which are assumed to be V''_{Ba}, compensate the donors. Under reducing conditions, electronic compensation is expected through the formation of Ti^{3+} as shown in Equation 10. The

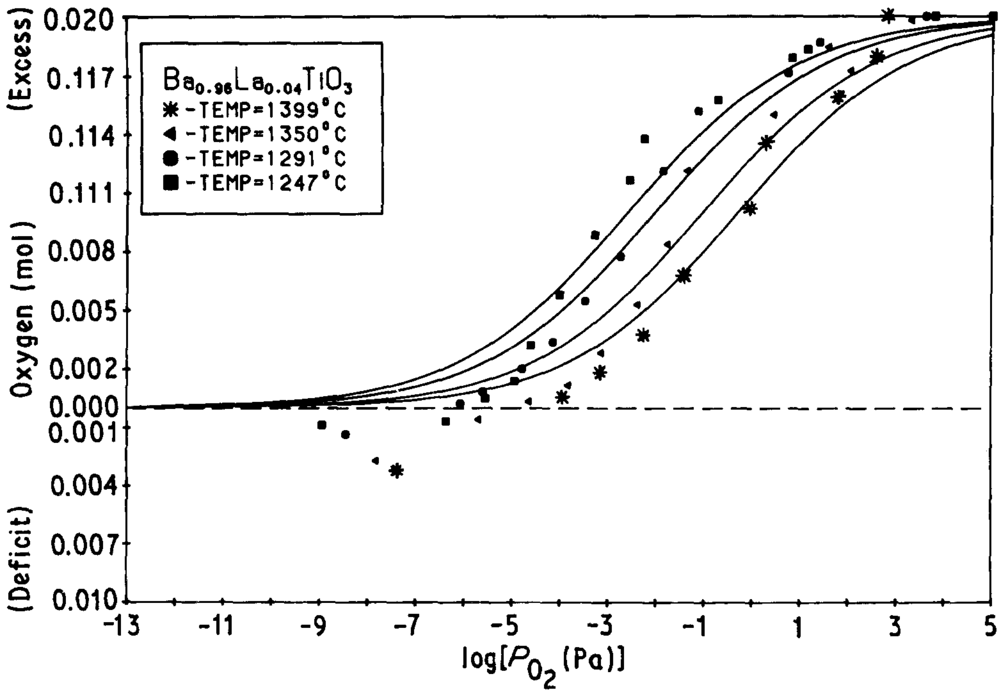

Figure 1 Plot of oxygen exchange against oxygen partial pressure for $Ba_{0.96}La_{0.04}TiO_3$ at different temperatures.

solid lines in Fig. 1 were calculated from the equilibrium constant expression of Equation 11. The experimental points agree quite well with the theoretical expression except at the most reducing conditions where additional oxygen loss occurs through the formation of native oxygen vacancies. This model does not take this loss into account. Fig. 1 further shows that the transition from ionic to electronic compensation occurs at higher oxygen activity as the temperature is increased, as has previously been observed [28] in the lanthanum-doped $SrTiO_3$ system.

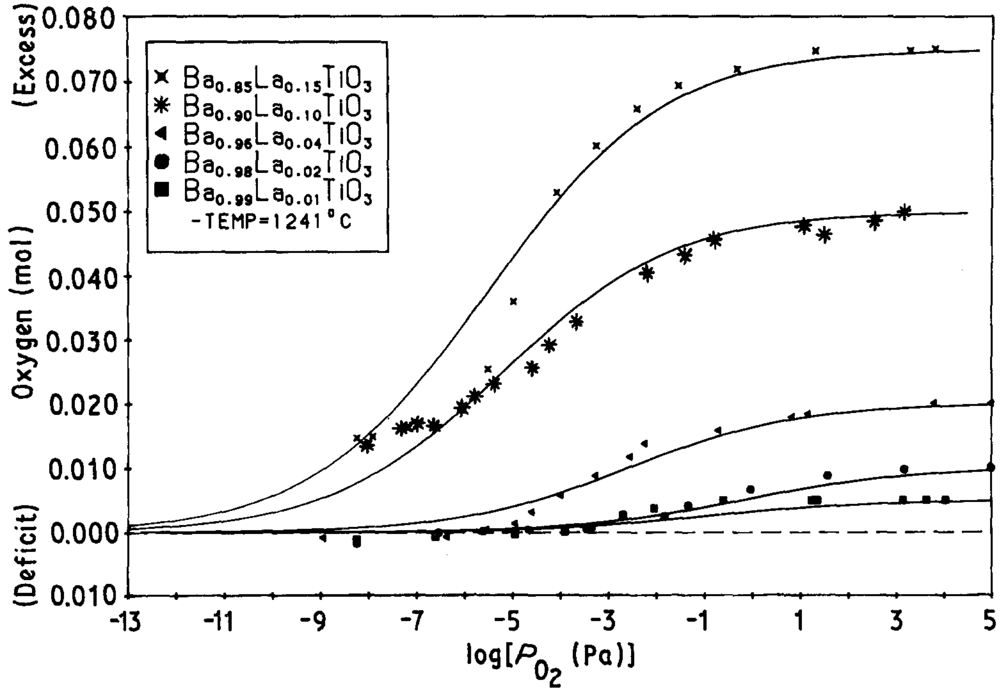

Figure 2 Plot of oxygen exchanges against P_{O_2} at 1241° C for different lanthanum contents in $BaTiO_3$.

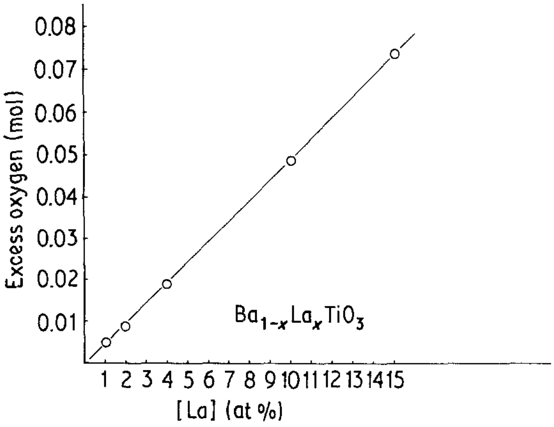

Figure 3 Plot of moles excess oxygen absorbed as a function of lanthanum content at 10^{-3} Pa.

The dependence of stoichiometric excess oxygen on lanthanum content and P_{O_2} is shown in Fig. 2 at 1241° C. As can be observed as the dopant concentration increases at any given P_{O_2}, the amount of excess oxygen also increases. This is illustrated by Fig. 3 which is a plot of excess oxygen, x, as a function of dopant content at 1241° C and 10^{-3} Pa P_{O_2}. This linear behaviour was observed throughout the range of temperatures studied.

TABLE I Change in enthalpy of reaction (ΔH) as a function of dopant

La_2O_3 (at %)	ΔH (kJ mol^{-1})
2	440
4	370
10	355
15	225

The relative defect concentration, as expressed in Equation 4, and determined from TGA data, is plotted in Fig. 4 as a function of oxygen activity at 1300° C, for several lanthanum contents. The quarter power dependence on oxygen activity predicted by Equation 14 is followed fairly well in the low P_{O_2} region where electronic compensation is expected. As can be seen, the transition from ionic to electronic compensation shifts to lower P_{O_2} as the dopant concentration increases. The influence of temperature is illustrated in Fig. 5, which is a plot of the TGA data for the 4 at % lanthanum-doped $BaTiO_3$. The slopes increase as temperature decreases, as predicted by Equation 14. Arrhenius plots of the equilibrium constants obtained from Fig. 5 and Equation 14 yield the enthalpy of reaction for reduction of lanthanum-doped $BaTiO_3$ (Reaction 9). Fig. 6 illustrates such a plot for 4 at % lanthanum-doped $BaTiO_3$ and Table I tabulates the data as a function of lanthanum content.

A continuous decrease in ΔH is observed as the dopant content increases to 15 at %. This is contrary to our earlier observation [28] on the lanthanum-doped $SrTiO_3$ system where a single value of ΔH was determined (with dopant content up to 20 at %). The change in ΔH observed in $BaTiO_3$ as the dopant content increases might be attributed to clustering or association of defects. For example, the previously mentioned Ruddleston–Popper shear planes that could be introduced in the lanthanum-doped $BaTiO_3$

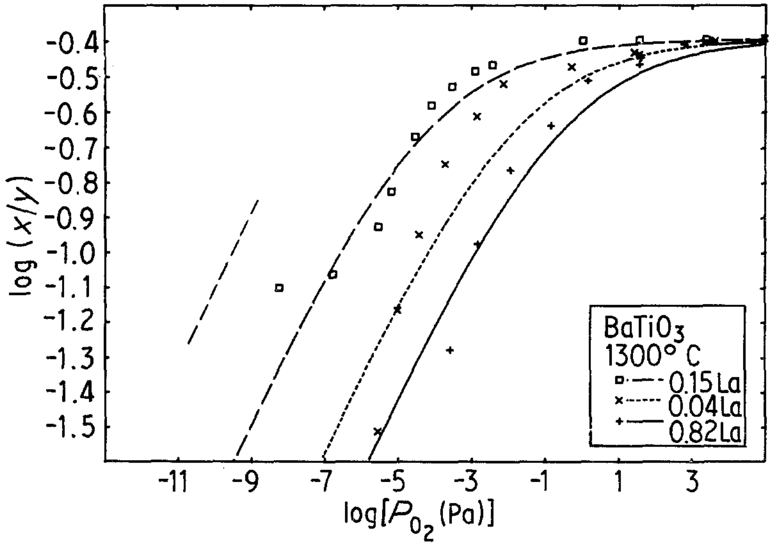

Figure 4 Relative defect concentration against P_{O_2} and lanthanum content at 1300° C.

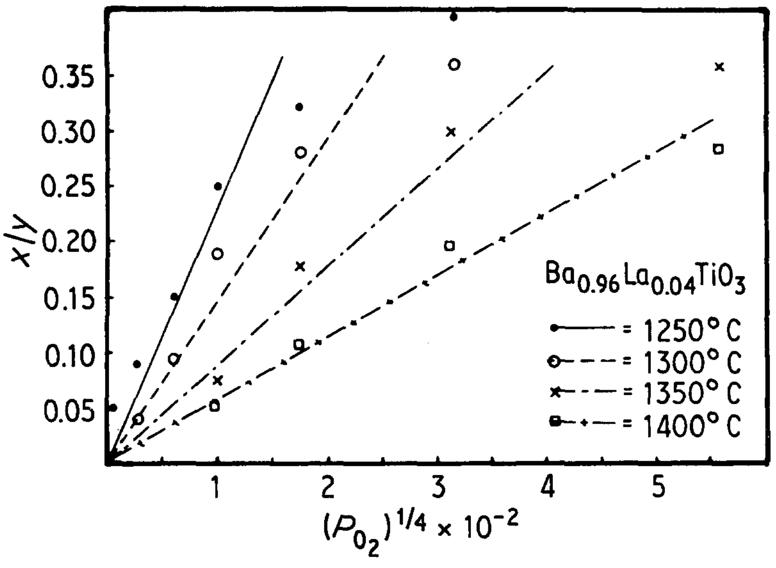

Figure 5 Plot of excess oxygen as a function of $P_{O_2}^{1/4}$ and temperature of 4 at% lanthanum doped $BaTiO_3$.

system due to stoichiometric excess of oxygen uptake at high oxygen activity, may interact with the A-site disorders of the perovskite $BaTiO_3$ in a manner similar to that suggested by Catlow [31]. Another possibility is that the extrinsic cation vacancies, introduced to compensate the donor dopant, may associate in the form of a complex with the donor. In this case the donor ion will have a lattice defect in its vicinity through which it may diffuse. The diffusion coefficient of the donor will accordingly be directly proportional to its concentration. Defect complexes in $BaTiO_3$ have been suggested [9] whereby,

$$V''_{Ba} + 2La^{\cdot}_{Ba} \rightleftarrows (V''_{Ba}, La^{\cdot}_{Ba}) + La^{\cdot}_{Ba} \quad (16)$$

or

$$V''_{Ba} + 2La^{\cdot}_{Ba} \rightleftarrows (La^{\cdot}_{Ba}, V''_{Ba}, La^{\cdot}_{Ba}) \quad (17)$$

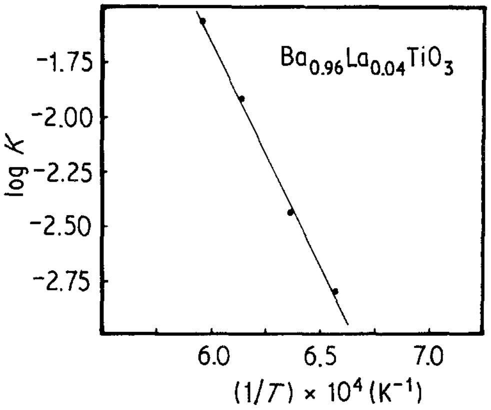

Figure 6 Plot of equilibrium constant as a function of temperature for 4 at% lanthanum-doped $BaTiO_3$.

The two member complex of Reaction 16 is more likely to occur due to entropy considerations [32]. The reported [33] activation energy for diffusion of barium in $BaTiO_3$ is 333.2 kJ mol^{-1}. This value is close to that measured here, which suggests agreement with such a model. However, further work is needed to identify positively the mechanism responsible for the change in ΔH. Also, it should be noted that the proposed model may be oversimplified and the dilute solution assumption may not be completely justified. The model certainly fits most of the data, but the incorporation of complexes as suggested above may yield a better correlation.

5. Conclusions

The TGA data support the proposed defect structure model for donor doped $BaTiO_3$. The donor dopant is substituted by a $Ti^{4+} \rightarrow Ti^{3+}$ transition at low oxygen activity, whereas, at high oxygen activity, stoichiometric excess of oxygen is incorporated into the system resulting in the possible exsolution of a barium-rich phase which introduces A-site vacancies in the perovskite lattice. The enthalpy of the redox reaction is found to be composition dependent, which might be interpreted in terms of clustering or association of defects.

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