



# The Defect Chemistry of Donor-Doped BaTiO<sub>3</sub>: A Rebuttal

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**Abstract.** It has recently been asserted that the donor charge in La<sup>+3</sup>-doped BaTiO<sub>3</sub> is always compensated by Ti vacancies, and that electrons are never the primary compensating defect. It was also stated that the conductivity observed in reduced, donor-doped BaTiO<sub>3</sub> results from the loss of a very small amount of oxygen not directly related to the donor content. However, the observed reproducible and reversible weight loss on reduction, or gain on oxidation, is exactly that expected for a change between ionic and electronic compensation. It corresponds to the loss or gain of the “excess” oxygen contained in the donor oxide, e.g. LaO<sub>1.5</sub> vs. the BaO it replaces. The amount of this weight change is proportional to the donor concentration. This is in agreement with the observation that the equilibrium conductivity in the P(O<sub>2</sub>)-independent region of electronic compensation is proportional to the donor concentration. Thus the conductivity observed in reduced samples is directly coupled to the donor concentration, and the carrier concentration is equal to the net donor content. In fact, the equilibrium conductivity of donor-doped BaTiO<sub>3</sub> conforms to the behavior expected from classical defect chemistry, and exhibits regions of both ionic and electronic compensation of the donor charge, as expected. Phase studies by TEM have shown that donor-doped BaTiO<sub>3</sub> sintered in air self-adjusts its composition, by splitting out a second phase if necessary, so that the appropriate amount of compensating Ti vacancies are formed. However, when sintered in a reducing atmosphere, the composition self-adjusts to accommodate charge compensation by electrons.

**Keywords:** BaTiO<sub>3</sub>, donor-doped, charge compensation, conductivity, phase equilibria

## Introduction

In a detailed study of donor(La<sup>+3</sup>)-doped BaTiO<sub>3</sub> published recently in this journal [1], Morrison, Coats, Sinclair, and West (which will be referred to as MCSW) proposed a defect chemistry model that differs significantly from previously proposed models. Their points can be summarized as follows:

1. Donors are charge-compensated by Ti vacancies under all circumstances, i.e. electrons never serve as the major charge-compensating species.
2. The conductivity that is observed in reduced samples results from the loss of a very small amount of oxygen that is unrelated to the donor content.
3. Previous measurements were not made under true equilibrium conditions.
4. There is serious disagreement between earlier studies, particularly those of Daniels and Härdtl [2] and Chan and Smyth [3]. The former will be referred to

as D and H, while the latter will be designated C and S.

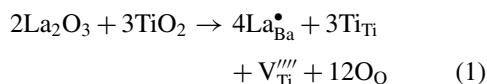
However, the first two proposals are in serious disagreement with earlier experimental results, some of which are not referenced or not discussed in MCSW. The purpose of this publication is to point out these discrepancies, and to show that the earlier model is in much better agreement with a large variety of observed behavior. It will be shown that electrons are in fact a major charge-compensating defect over a wide range of conditions, and that the conductivity in reduced samples is due to an electron concentration that is directly coupled to the donor concentration. The question of equilibrium conditions will be addressed, and it will be shown that there is no serious inconsistency between the work of D and H and of C and S. The earlier defect model has been recently reviewed [4].

MCSW prefer to limit the expression “donor impurity” to an impurity that is primarily

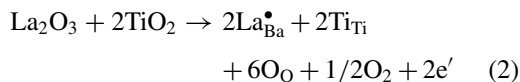
charge-compensated by electrons. This is a bit ambiguous when the same donor can be compensated by either electrons or lattice defects, depending on the equilibration conditions. I prefer a more general definition; one that includes any incorporated impurity that results in a greater positive charge than normally found at the occupied site. That will include impurity cations that have a higher positive charge than the cation they replace, impurity anions that have a lesser negative charge than the anion they replace, or any cation in an interstitial position. In all of these cases the electron concentration will be increased over that in the undoped oxide, whether or not the electrons are the major charge-compensating defect. In this paper we will deal only with the case of substitutional impurity cations that have a higher charge than the cation they replace.

### Thermogravimetric Evidence

As just defined, a donor oxide has more oxygen atoms per cation than does the host binary oxide it replaces, e.g.  $\text{LaO}_{1.5}$  vs. the  $\text{BaO}$  it replaces in the lattice. The two limiting cases for the mechanism of donor incorporation depend on the fate of that "extra" oxygen. If it is retained in the lattice, then the donor centers are charge-compensated by ionic defects, cation vacancies or anion interstitials. For La-doped  $\text{BaTiO}_3$  with Ti vacancies as the charge-compensating defect, the incorporation reaction can be written as:



If the extra oxygen is expelled, then the donor centers are charge-compensated by electrons:



These two limiting cases are connected by an exchange reaction:



where the excess  $\text{TiO}_2$  would be expected to be largely expelled as  $\text{Ba}_6\text{Ti}_{17}\text{O}_{40}$ . We assume that Ti vacancies and oxygen vacancies are the only significant lattice

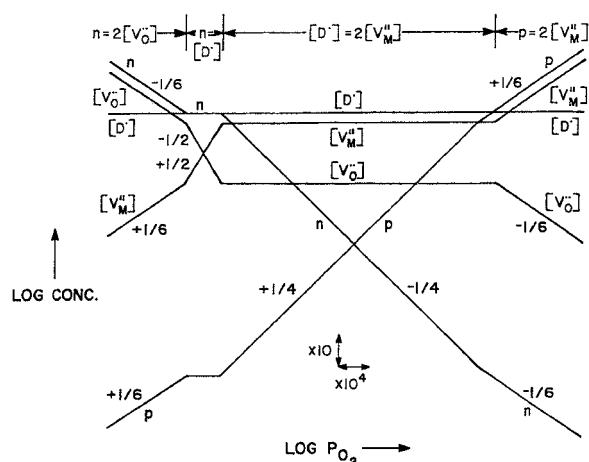


Fig. 1. A Kröger-Vink diagram for a hypothetical oxide, MO, donor-doped with  $\text{D}_2\text{O}_3$ . Adapted from Fig. 5 of [6].

defects, as indicated experimentally [5], and in agreement with MCSW. Clearly, electrons are favored by reducing conditions, oxygen loss, while Ti vacancies are favored by oxidation, oxygen gain. This is shown in Fig. 1, a Kröger-Vink diagram of a generic donor-doped oxide, MO [6]. This diagram demonstrates that there will *always* be two regions in which charge neutrality is dominated by the impurity. (Fig. 1 represents the case that Schottky defects are the favored form of intrinsic ionic disorder, and that the concentration of intrinsic ionic defects exceeds that of intrinsic electronic defects. The opposite case is also shown in [6] and demonstrates that the essential points remain the same.) In the higher range of oxygen activities, the donor will be primarily charge-compensated by a product of oxidation. In  $\text{BaTiO}_3$  that defect is the Ti vacancy [5]. As the oxygen activity is decreased, the concentration of a product of reduction will increase until it takes over the dominant role in charge neutrality, in this case electrons. Thus there are not two different models, one in which Ti vacancies are the compensating defect and one in which electrons play that role. They are both part of the same model. It is just a question of which part of the overall behavior is observed within a given range of experimental parameters. It will be shown that the experimental results for donor-doped  $\text{BaTiO}_3$  fit this unified model quite well. The defect chemistry of doped perovskites has been recently reviewed in some detail [7].

As donor-doped  $\text{BaTiO}_3$  is reduced, and the compensating defect changes from Ti vacancies to

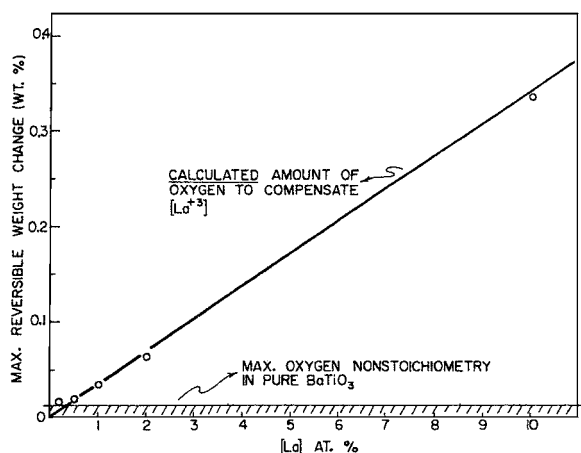


Fig. 2. The reversible weight change between oxidized and reduced BaTiO<sub>3</sub> doped with various concentrations of La<sup>+3</sup>. The line is the calculated weight change for gain or loss of the "extra" oxygen in the donor oxide. Adapted from Fig. 2 of [8].

electrons, according to Eq. (3) there should be a loss of an amount of oxygen that is the charge equivalent of the donor content, while there should be a weight gain by the same amount for the reverse reaction. MCSW assert that "The amount of oxygen loss is small,  $\ll 1\%$ , and difficult to quantify by thermogravimetric techniques, —". In fact that measurement has been done on La-doped BaTiO<sub>3</sub> [8], and the reversible weight change is precisely that expected for weight gain or loss of oxygen that is the charge equivalent of the donor content, as shown in Fig. 2. The loss of an amount of oxygen that is the charge equivalent of the donor content will leave behind an electron concentration that is equal to the donor concentration. The electrons have then become the main charge-compensating defect. In that work, sintered samples with compositions Ba<sub>1-x</sub>La<sub>x</sub>TiO<sub>3</sub> and BaTi<sub>1-y</sub>Nb<sub>y</sub>O<sub>3</sub>, with  $x$  up to 0.1 and  $y$  up to 0.02 were equilibrated alternately in pure oxygen or CO at 1060°C. At least duplicate samples were quenched in the ambient gas and then weighed at room temperature on a Cahn RG microbalance. There was a correlation of better than 90% between the measured reversible weight change and the amount calculated according to Eq. (3). In addition to the results reported in [8], the same type of result has been obtained for La-doped SrTiO<sub>3</sub> [9, 10], Ta-doped SrTiO<sub>3</sub> [11], La-doped CaTiO<sub>3</sub> [12], and Ta-doped CaTiO<sub>3</sub> [13]. For the latter four cases, the reducing atmosphere was a CO/CO<sub>2</sub> mixture adjusted to an oxygen activity of 10<sup>-15</sup> or

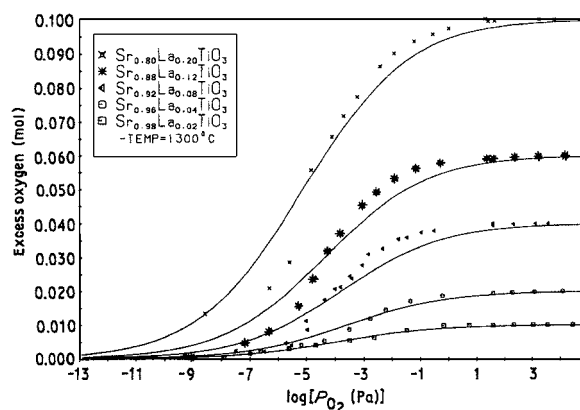


Fig. 3. The reversible weight change between oxidizing and reducing equilibrations at 1300°C for La<sup>+3</sup>-doped SrTiO<sub>3</sub>, as a function of La<sup>+3</sup> concentration and the oxygen activity. Adapted from Fig. 2 of [9].

10<sup>-16</sup> atm at 1050 or 1100°C. In the first-mentioned case [9], the weight change was measured at the equilibration temperature as a function of La content (2–20%), temperature (50 degree intervals between 1200 and 1400°C), and oxygen activity (stepwise changes from 10<sup>-2</sup> to 10<sup>-18</sup> atm). These works indicate that the compensation mechanism moves between Eqs. (1) and (2) for oxidizing and reducing conditions, respectively. The measurements made at temperature as a function of oxygen activity for several donor concentrations are shown in Fig. 3 and clearly demonstrate the transition in the amount of "excess" oxygen between the two limiting cases [9]. These measurements are in agreement with the work of Johnston and Sestrich [14] who found that the chemical reducing power, i.e. the free electron concentration, of La-doped BaTiO<sub>3</sub> equilibrated in reducing atmospheres is proportional to the La concentration.

These results show that electrons can indeed be the major charge-compensating defect for the donor content. It is also clear that the conductivity observed in reduced, donor-doped BaTiO<sub>3</sub> is not due to the loss of just a small amount of oxygen that is unrelated to the donor content. The results just described indicate that the conductivity arises from an electron concentration that is directly coupled to the donor content.

### Evidence from Equilibrium Conductivities

MCSW mention the early study of donor-doped BaTiO<sub>3</sub> by D and H [2], but omit one of their important

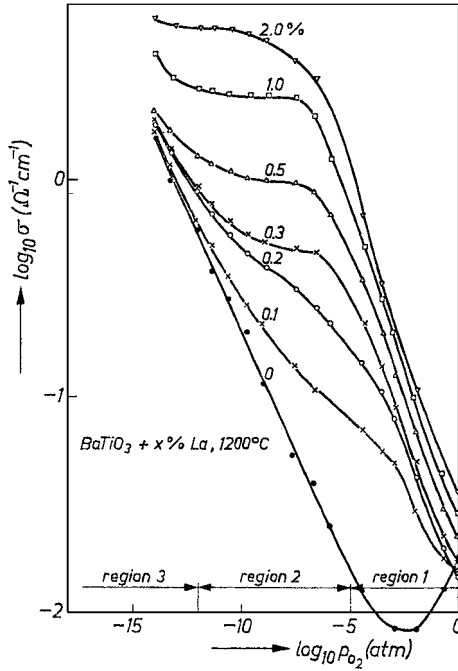
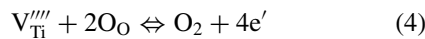


Fig. 4. The equilibrium conductivity of donor-doped BaTiO<sub>3</sub> at 1200°C as a function of oxygen activity for several concentrations of La<sup>3+</sup>. Adapted from Fig. 2 of [2].

observations. These authors measured the equilibrium conductivity of sintered samples as a function of oxygen activity at 1200°C with La contents from 0.1 to 2%, as shown in Fig. 4. The results show that as the oxygen activity decreases from 1 atm there is first an increase in the conductivity with a log-log slope of  $-1/4$ . This then flattens out into a plateau whose level increases with increasing donor concentration. Below the plateau the conductivities of all samples return to an increasing conductivity that seems to be converging toward a common slope. This is exactly the behavior expected for a donor-doped oxide as shown in Fig. 1 [6].

The initial reduction reaction involves the consumption of Ti vacancies and their replacement with electrons:



Which has the mass action expression:

$$K_{\text{red}} = n^4 P(\text{O}_2) / [V_{\text{Ti}}^{\prime\prime\prime}] \quad (5)$$

Just below an oxygen activity of 1 atm, Ti vacancies are the major charge-compensating defect and the

approximate condition of charge neutrality is

$$[\text{La}_{\text{Ba}}^{\bullet}] = 4[V_{\text{Ti}}^{\prime\prime\prime}] \quad (6)$$

Combination of Eqs. (5) and (6) gives

$$n = (4K_{\text{red}}[\text{La}_{\text{Ba}}^{\bullet}])^{1/4} P(\text{O}_2)^{-1/4} \quad (7)$$

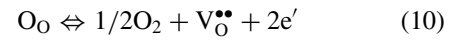
This is in agreement with the observed log-log slope and the small dependence on the donor concentration. When the electron concentration reaches the donor concentration, the electrons become the major charge-compensating defect and the approximate condition of charge neutrality changes to:

$$[\text{La}_{\text{Ba}}^{\bullet}] = n \quad (8)$$

Combination of (5) and (8) gives:

$$[V_{\text{Ti}}^{\prime\prime\prime}] = [\text{La}_{\text{Ba}}^{\bullet}]^4 P(\text{O}_2) / K_{\text{red}} \quad (9)$$

This shows that the Ti vacancy concentration drops off very quickly with decreasing oxygen activity in this region. Note that the electron concentration should be proportional to the donor concentration in this region. At even lower oxygen activities the concentration of defects created by reduction exceed the donor concentration. The reduction reaction is then:



which has the mass-action expression:

$$K_n = [V_{\text{O}}^{\bullet\bullet}] n^2 P(\text{O}_2)^{1/2} \quad (11)$$

and the condition of charge neutrality becomes:

$$n = 2[V_{\text{O}}^{\bullet\bullet}] \quad (12)$$

Combination of Eqs. (11) and (12) gives the familiar expression:

$$n = (2K_n)^{1/3} P(\text{O}_2)^{-1/6} \quad (13)$$

A key observation of Daniels and Härdtl is shown in Fig. 5, adapted from their publication [2]. The conductivity in the plateau region is proportional to the donor concentration, as expected from Eq. (8), and can be quantitatively expressed as:

$$\sigma = [\text{La}_{\text{Ba}}^{\bullet}] e \mu \quad (14)$$

where  $\mu$  is the electron mobility taken to be 0.1 cm<sup>2</sup>/v sec, a value in good agreement with other experimental determinations. Equation (14) confirms that Eq. (8)

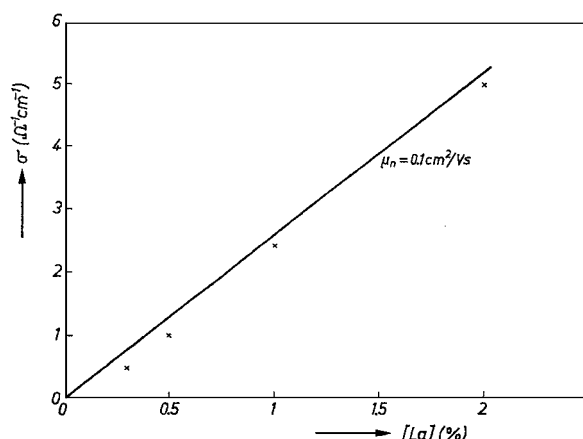


Fig. 5. The equilibrium conductivity of donor-doped BaTiO<sub>3</sub> at 1200°C in the P(O<sub>2</sub>)-independent region as a function of the La<sup>+3</sup> concentration. The line represents the conductivity calculated from [La<sub>Ba</sub><sup>•</sup>]<sub>e</sub>(0.1 cm<sup>2</sup>/v sec). Adapted from Fig. 3 of [2].

is the correct approximation to charge neutrality in this region, and that electrons have become the major charge-compensating defect. It also confirms that the observed conductivity in reduced material is directly coupled to the donor content, and results from the loss of the “extra” oxygen brought in by the donor oxide.

MCSW assert that there is serious disagreement between the results and model of D and H [2], and of those reported by C and S [3]. In particular, they state that the model of C and S “predicts electronic compensation and semiconductivity under all conditions.” However, the work of C and S was deliberately focused on the small concentrations of donor that give conducting material when cooled rapidly enough in air to quench in the high temperature equilibria. The abstract states that “Donor additions to BaTiO<sub>3</sub> up to a few tenths atom percent are compensated by electrons.” That is a correct statement. C and S used donor concentrations of 0.006 to 0.16%, while D and H used concentrations of 0.1 to 2%. It is easily shown that P(O<sub>2</sub>)<sup>o</sup>, the oxygen activity at the transition from electronic to ionic compensation, moves toward higher oxygen activities with decreasing donor concentration according to the relationship

$$P(O_2)^o = K_{red}/4[La_{Ba}^{\bullet}]^3 \quad (15)$$

The data of D and H clearly show that the region of ionic compensation is becoming more narrow with de-

creasing donor concentration, while the data of C and S show a drop-off from the plateau as the oxygen activity approaches 1 atm for the highest donor concentrations used in their study, indicating that ionic compensation is coming into play. Thus D and H show ionic compensation disappearing while C and S show it appearing as their respective donor concentration ranges converge toward each other. There is no significant disagreement here. It is just that the region of ionic compensation has moved almost entirely out of the observable range for the donor concentrations used by C and S. Later work by Chan, Harmer, and Smyth on samples with higher donor concentrations (6% Nb) clearly show that Ti vacancies are the major compensating defect under oxidizing conditions, while electrons are the compensating defect at lower oxygen activities [5]. It is of course elementary that electronic compensation of donors will give way to ionic compensation under sufficiently oxidizing conditions. However, “sufficiently oxidizing conditions” may not always be readily accessible experimentally.

### The Question of Equilibrium

MCSW deal quite extensively with the question of whether the various measurements have been made under truly equilibrium conditions. The simple answer is that it is very unlikely that any of them were. It is improbable that any of the very extensive studies of BaTiO<sub>3</sub> involved full thermodynamic equilibrium, but that does not mean that the measurements are not useful if properly interpreted. The Ba/Ti ratio is generally fixed rather than being determined by any equilibrium process. It is possible that some measurements have been made in the presence of an adjacent second phase, either Ba<sub>6</sub>Ti<sub>17</sub>O<sub>40</sub> or Ba<sub>2</sub>TiO<sub>4</sub>, but even then it is doubtful that cation equilibrium is maintained during the changes in temperature and oxygen activity typical of high temperature measurements. This issue of cation equilibria in ternary compounds has been dealt with in earlier literature [15–17]. The impurity content, whether accidental background impurities or deliberately added dopants, is not in equilibrium with anything. In many cases we have to be satisfied with maintaining oxygen equilibria while all of the other constituents remain at constant concentration. As long as oxygen equilibria can be attained such that reproducible states can be achieved, meaningful thermodynamic interpretations can be obtained.

MCSW question whether or not the equilibrium conductivity measurements made on donor-doped BaTiO<sub>3</sub> were truly at equilibrium. Since the oxygen vacancy concentration is strongly suppressed by the donor content, oxygen diffusion is accordingly much slower than in acceptor-doped or undoped BaTiO<sub>3</sub>. D and H state that “After each variation of the atmosphere the conductivity tended more or less rapidly to the new equilibrium value. —if the conductivity no longer changed, it was assumed that the state of equilibrium had been attained. *This state proved to be attainable reversibly from higher or from lower partial pressures.*” We took similar precautions with our own measurements. The data were checked periodically to ensure that it could be reproduced from different starting values of temperature and oxygen activity. So within the time scale of these measurements, it seems certain that oxygen equilibrium had been attained. This does not preclude a longer time scale for equilibria of other types, such as adjustment of cation activities to new equilibration conditions. That may account for equilibration times of up to four months that MCSW attribute to Nowotny and Rekas [18], although they did not indicate whether the changes over such long times were reversible. They could also result from equilibration of the sample with the impurity content of the experimental apparatus, or from diffusion of the electrode material, usually Pt, into the sample.

The conditions under which donor-doped BaTiO<sub>3</sub> can be conducting at room temperature receives considerable attention from MCSW. In particular they disagree with our observation that lightly doped BaTiO<sub>3</sub> can be conducting after having been sintered in air. There is a very practical resolution to this issue. When the author was with the Sprague Electric Company many years ago, they manufactured a capacitor that was based precisely on that phenomenon. The Hypercon capacitor consisted of BaTiO<sub>3</sub>, doped with a few tenths of a percent donor, Nb I believe, that was sintered *in air*, and which, after fairly rapid cooling gave a black, conducting body. These were then heated, *in air*, at a temperature considerably lower than that at which they had been sintered. This resulted in the transformation of a thin surface layer to an insulating state. Electrode paste was fired on (this may have been simultaneous with the superficial oxidation), and this resulted in a capacitor in which one electrode is the conducting interior of the sintered body. This process is possible because electronic compensation is favored by high temperatures, while ionic compensation is favored by low

temperatures. This is shown quantitatively by Eq. (15), since the oxygen activity at the boundary between ionic and electronic compensation,  $P(\text{O}_2)^\circ$ , is proportional to  $K_{\text{red}}$ , the mass-action constant for the reduction reaction, which increases with temperature. In the equilibrium conductivity the electron concentration in the region of ionic compensation (log-log slope of  $-1/4$ ) rises with increasing temperature. This means that the electron concentration reaches the level of the donor concentration at successively higher oxygen activities with increasing temperature until this intersection point passes above the oxygen activity of air. At that point the donors are compensated by electrons, and the material will be semiconducting if cooled rapidly enough to avoid the reoxidation that occurs at lower temperatures where the region of electronic compensation has passed below the oxygen activity of air.

Thus the apparent disagreement can be resolved by careful consideration of the donor concentration and the kinetics of equilibration. For material sintered in air, BaTiO<sub>3</sub> with up to a few tenths of a percent donor will be dark-colored and conducting if cooled rapidly. If it is cooled slowly or annealed at a lower temperature, it may be superficially or completely oxidized to an insulating state before the composition becomes kinetically frozen. For higher donor concentrations, material processed in air will be insulating, and will become conducting only if sufficiently reduced. The reduction eventually results in the electron concentration rising to the donor concentration, as discussed above.

Further information on the type of charge compensation is given in the studies of phase equilibria by Chan, Harmer, and Smyth (CHS) [5]. In this study, donor-doped samples were prepared with the Ba and Ti contents adjusted to precisely accommodate the various possible compensating defects. The samples were sintered at 1450°C for 5 hours in either air or nitrogen to represent oxidizing and reducing conditions, respectively. The donor was 0.25 or 6% Nb, with the latter concentration receiving most of the attention. Ion-thinned samples were then examined by TEM for the presence of second phases. The second phases, and their identification as Ba-rich or Ti-rich, were easily observed in the samples with 6% donor. The results can be summarized as follows:

BaTi<sub>0.926</sub>Nb<sub>0.06</sub>O<sub>3</sub>: allows for  $[\text{Nb}^\bullet_{\text{Ti}}] = 4[V'''_{\text{Ti}}]$   
 Sintered in air: single phase  
 Sintered in N<sub>2</sub>: Ba-rich second phase

Ba<sub>0.97</sub>Ti<sub>0.94</sub>Nb<sub>0.06</sub>O<sub>3</sub>: allows for  $[\text{Nb}_{\text{Ti}}^{\bullet}] = 2[\text{V}_{\text{Ba}}'']$

Sintered in air: Ti-rich second phase

BaTi<sub>0.94</sub>Nb<sub>0.06</sub>O<sub>3</sub>: allows for  $[\text{Nb}_{\text{Ti}}] = n$  (or compensation by  $\text{O}_i''$  or equal amounts  $\text{V}_{\text{Ba}}''$  and  $\text{V}_{\text{Ti}}''''$ . Both considered unlikely)

Sintered in air: Ti-rich second phase

Sintered in N<sub>2</sub>: single phase

BaTi<sub>0.0075</sub>Nb<sub>0.0025</sub>O<sub>3</sub>: allows for  $[\text{Nb}_{\text{Ti}}^{\bullet}] = n$  (or  $\text{O}_i''$ , or  $[\text{V}_{\text{Ba}}''] = [\text{V}_{\text{Ti}}'''']$ )

Sintered in air: single phase

Thus for the samples with 6% Nb, when sintered in air, the samples split out a Ti-rich phase so that compensation could be by Ti vacancies, except when the composition had the right amount of Ti vacancies built in. However when sintered in N<sub>2</sub>, the sample with built-in Ti vacancies split out a Ba-rich second phase in order to adjust the Ba/(Ti + Nb) ratio back to unity as is appropriate for electronic compensation. For the sample with no built-in cation vacancies, when sintered in air, a Ti-rich second phase appeared so that compensation could be by Ti vacancies. However, when sintered in N<sub>2</sub>, the material was single phase, as expected for electronic compensation. The sample with 0.25% Nb, with no built in cation vacancies, was single phase when sintered in air, indicating compensation by electrons. It would have been nice to have examined a sample with this donor concentration with built-in Ti vacancies; one would expect to see a Ba-rich second phase, but that experiment was not performed. To summarize: with 6% Nb all samples sintered in air had charge-compensation by Ti vacancies, but when sintered in N<sub>2</sub> the charge compensation was by electrons. With 0.25% Nb, charge compensation was by electrons even when sintered in air. Even the modest reducing power of N<sub>2</sub>, which typically has about 10 ppm O<sub>2</sub>, i.e. about 10<sup>-5</sup> atm as measured by a zirconia cell, was sufficient to cause the oxygen loss that results in charge compensation by electrons according to Eq. (3).

We believe that the key to this experiment was that the phase content was established during the sintering process while the lattice is in a state of flux as a result of densification and grain growth. This allowed any second phases to concentrate, primarily at the triple points between grains, where they were easily detected. There were no attempts to change the phase distribution after sintering by subjecting the samples to oxidizing or reducing anneals. That would require a substantial amount of cation diffusion which is, of course, a very slow process. It appears that in the similar studies by

MCSW, that the equilibration conditions of presintered samples were changed, in which case any phase separation would require substantial cation diffusion in the solid state.

## Summary

The principle involved in this discussion of charge compensation in donor-doped BaTiO<sub>3</sub> is most easily described with the help of a Kröger-Vink diagram for a simpler system, as shown in Fig. 1. This is a diagram for a hypothetical oxide MO for which the preferred type of intrinsic ionic disorder is Schottky disorder, i.e. equal concentrations of cation and anion vacancies. On the oxidized side of the extrinsic region, the donor impurities must be charge-compensated by a negatively charged product of oxidation, cation vacancies in this case. Because the mass-action expression for Schottky disorder requires that the product of the concentrations of cation and anion vacancies be a constant at a given temperature, the anion vacancy concentration must be depressed by a factor similar to that by which the cation vacancy concentration is increased. As the oxygen activity is decreased, the electron concentration is increasing until it reaches the donor concentration. It cannot initially increase further with reduction because there are no oppositely charged species to increase with it to maintain charge neutrality. It must hold at the donor level until the increasing concentration of oxygen vacancies approaches the donor level. The region over which this process is occurring corresponds to the region where the donors are compensated by electrons. Only with further reduction can the electron and oxygen vacancy concentrations rise together with the characteristic log-log slope of -1/6. The point of this is that because the presence of the donors causes a suppression of the concentration of oxygen vacancies in the region of ionic compensation, there *must* be a region of electronic compensation between the region of ionic compensation and the region where electrons and oxygen vacancies are the major contributors to charge neutrality. For the example shown in Fig. 1 the width of the region of electronic compensation appears narrow, but it is actually four orders of magnitude of oxygen activity. It is that narrow because the donor concentration was chosen to be only one order of magnitude greater than the concentration of intrinsic cation vacancies. In the case of donor-doped BaTiO<sub>3</sub> that factor is generally much larger. For the

example shown in Fig. 1, the width of the region of electronic compensation is four orders of magnitude larger than the factor by which the donors increased the cation vacancy concentration above its intrinsic value. It has been shown earlier in this paper that the experimental results are in excellent agreement with this general picture. This is specifically supported by the observation that the electron concentration in the plateau region is equal to the donor concentration, Fig. 5, and that the reversible weight change due to gain and loss of oxygen between the oxidized and reduced states corresponds to the excess oxygen brought into the system by the donor oxide relative to the binary component oxide it replaces, Fig. 2.

It should be possible to represent a valid equilibrium defect model by a Kröger-Vink diagram of the type shown in Fig. 1. That is not possible with the model proposed by MCSW.

Phase analysis by TEM examination of thinned samples show that for samples with 6% donor sintered in air, the only single phase composition is that in which the appropriate amount of Ti vacancies for compensation of the donor is built-in [5]. For other compositions, the system splits out a Ti-rich phase in order to leave the correct amount of compensating Ti vacancies in the bulk. For samples sintered in N<sub>2</sub>, the only single phase composition is that with both cation sublattices exactly filled. That is the situation expected when the donors are compensated by electrons.

The well-known anomaly in the room temperature resistivity of donor-doped BaTiO<sub>3</sub> is still not well understood. The anomaly is that while the resistivity initially decreases rapidly with increasing additions of donor, after a few tenths of a percent of donor further increases cause a rapid reversion to insulating properties. The change in properties is much too abrupt to be accounted for by conventional defect chemistry. (The sudden change in the room temperature resistivity of acceptor-doped BaTiO<sub>3</sub> as a function of oxygen activity of equilibration results from the trapping of holes by the oppositely charged acceptor centers. No comparable situation is apparent in the donor-doped case.) The phenomenon is clearly related to the effective equilibration conditions as affected by cooling rates and annealing processes. There is also a marked change in microstructure that will affect equilibration kinetics. In the samples with small additions of donors, the grain size is tens of microns, similar to that of undoped or acceptor-doped material, while for the larger donor concentrations the grain size is about a micron, unless

the samples are sintered in reducing atmospheres, in which case the grains are again large. Thus it has been suggested that the small grain size correlates with conditions that lead to donor compensation by Ti vacancies [5].

Both D and H and C and S have shown that the equilibrium conductivity data for donor-doped BaTiO<sub>3</sub> are reversible and can be reproduced regardless of the direction of change of temperature and oxygen activity [2, 3]. This indicates that the oxygen activity within the sample has achieved equilibrium with that in the ambient. Moreover, the fact that regions with both ionic and electronic compensation of the donors are observed indicates that some form of cation vacancy equilibrium has also been maintained. This is supported by the measurements of the reproducible weight changes that result from oxidation or reduction of donor-doped BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and CaTiO<sub>3</sub> [8–13]. These weight changes correspond to the gain or loss of oxygen as the system changes from ionic to electronic compensation of the donors. Apparently there is enough cation diffusion, even at 1000°C to support these changes.

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