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# Effect of oxygen sublattice order on conductivity in highly defective fluorite oxides

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## Abstract

The study of ionic transport in cubic bismuth oxides is important technically because these materials exhibit the highest oxygen–ion conductivity of any material known to date. From a scientific point of view, the study of ionic transport in cubic bismuth oxides also provides an understanding of how anion transport in oxides with the fluorite structure is influenced by high vacancy concentration and how this is influenced by local structure. Bismuth oxide doped with isovalent rare earth cations retains the high temperature defective fluorite structure upon cooling down to room temperature. However, these doped materials undergo an order–disorder transition of the oxygen sublattice at about 600 °C. When annealed at temperatures less than the transition temperature the oxygen sublattice continues to order, and consequently oxygen ion conductivity undergoes a decay. However, the conductivity activation energies of the ordered structures after extended aging at 500 °C were observed to be lower than those of the structures prior to aging. Modeling of ordered structures based on TEM diffraction patterns indicates a $<111>$ vacancy ordering in the anion sublattice (occupancy ordering). Neutron diffraction studies show additional structural changes in the oxygen sublattice due to positional ordering. These studies indicate that the ionic conductivity is dependent on the distribution of oxygen ions between the regular 8c sites and the interstitial 32f sites in the fluorite structure. Based on the TEM and neutron diffraction studies and conductivity of ordered and disordered structures the influence of local structure on conductivity is described. These results indicate that ordering of anion vacancies in $<111>$ is common to fluorite oxides at high vacancy concentrations. Further, that the tendency to order depends on the dopant radii and polarizability.

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## 1. Introduction

It is well known that the conductivity of oxides such as $ZrO_2$ stabilized in the fluorite structure by lower valent dopants (e.g., $Y_2O_3$ and CaO) increases with increasing dopant concentration in the dilute (low dopant concentration) regime. This increase in conductivity is due to the increase in concentration of charge compensating anion vacancies ($Vo^{\bullet\bullet}$), the conducting species in these materials. It is also well known that the conductivity reaches a maximum at about 8–10 mole%, depending on the dopant. The ensuing decrease in conductivity with increasing dopant concentration is due to ordering of the anion sublattice. This ordering occurs in part because the concentration of $Vo^{\bullet\bullet}$ is no longer in the dilute limit and $Vo^{\bullet\bullet}$–$Vo^{\bullet\bullet}$ interactions have a higher statistical probability. Further, dopant-vacancy interactions (e.g., $Y_{Zr}'$–$Vo^{\bullet\bullet}$) also have a higher probability of occurrence.

For sometime the conventional wisdom had been that for yttria stabilized zirconia (YSZ), increasing $Y_{Zr}'$ concentration resulted in associated defects $(Y_{Zr}'–Vo^{\bullet\bullet})^{\bullet}$ at low $Y_{Zr}'$ concentration and $(Y_{Zr}'–Vo^{\bullet\bullet}–Y_{Zr}')^{x}$ at higher $Y_{Zr}'$ concentration.[1–3] These dopant-vacancy associated defects were responsible for the decreasing conductivity with increasing dopant concentration and were due to the Coulombic attraction between the negatively charged dopant and positively charged anion vacancy. However, recent studies with high resolution X-ray and neutron techniques have indicated a more

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complex situation involving vacancy clustering and a dopant radii dependence on associated defects.[4–6]

With respect to the later point, the work of Li et al.[4] indicates that for $M^{3+}$ dopant radii less than the host $Zr^{4+}$ cation radii the oxygen vacancies associate with the dopant, consistent with expectations based on electrostatic considerations. However, for $M^{3+}$ dopant radii greater than the host $Zr^{4+}$ cation radii the oxygen vacancies associate with the host cation. For YSZ, since the radii of $Y^{3+}$ is greater than $Zr^{4+}$, the vacancy associates that are formed are $(\mathrm{Zr}_{\mathrm{Zr}}^{x}\text{-}\mathrm{Vo}^{\bullet\bullet}\text{-}\ \mathrm{Zr}_{\mathrm{Zr}}^{x})^{\bullet\bullet}$ and the Y are 8-fold coordinated with O, in direct contrast to the expectation based on electrostatic considerations.

Therefore, there is a competition between electrostatic attraction, due to the difference in cation oxidation states, and structural considerations, due to the difference in cation radii, that determine whether the vacancy associates with the host or dopant cation. First principles calculations by Bogicevic et al. indicate that in this competition structural considerations dominate.[7] If for large radii dopants the vacancies associate with the host cations, then the decrease in conductivity with increasing dopant concentration is not due to dopant-vacancy associates and must be due to some form of ordering of the charge compensating vacancies at high vacancy concentrations.

Bogicevic et al.'s calculations show that vacancies repel each other but that they have a tendency to align as third nearest neighbors along <111> directions.[7] Thus, increasing vacancy concentrations would tend to result in <111> ordered arrays of oxygen vacancies. Similarly, Goff et al. has shown that vacancy clusters form and proposed that the decrease in conductivity with increasing vacancy concentration is due to the formation of "static aggregates".[5]

$Bi_2O_3$ stabilized in the fluorite structure by isovalent cations has an extremely high concentration of $\mathrm{Vo}^{\bullet\bullet}$ (25% of the anion sites) and no electrostatic difference between host and dopant cations. As such, cubic bismuth oxides provide an excellent model of how anion transport in oxides with the fluorite structure is influenced by high vacancy concentration and structural considerations in the absence of Coulombic attraction.

We have studied the effect of anion sublattice structure on conductivity in cubic $Bi_2O_3$ extensively.[8–19] The results of these investigations are reviewed here and used to explain the more general case of effect of anion sublattice structure on conductivity in fluorite oxides.

## 2. Conductivity decay

The high temperature cubic bismuth oxide stabilized with Lanthanide dopants undergoes an order–disorder transition of the anion sublattice at about 600 °C. Above the transition temperature the conductivity exhibits a low activation energy ($E_A$) due to the disordered anion sublattice, and below the transition temperature the conductivity exhibits a higher $E_A$ due to ordering of the anion sublattice. This ordering of the lattice below the transition temperature is time dependent. Thus when phase-stabilized cubic bismuth oxides are annealed at temperatures below the transition temperature, the oxygen ion conductivity undergoes a decay. This conductivity decay and associated structural change are fully reversed upon heating above the order–disorder transition temperature.

The aging phenomenon is distinct from a conventional crystallographic phase transformation. It is apparent as a degradation of conductivity with time.[8–10] It is revealed by an endotherm from DSC (or DTA) thermal analysis.[8–10] It results in formation of a superstructure observable by TEM diffraction patterns[11–13] and ordering of the oxygen sublattice as observed by neutron diffraction.[14,15] Yet all of these observations occur without the indication of a phase transformation by XRD.

### 2.1. *Effect of dopant radii, concentration and polarizability*

In order to better understand how different dopants affect conductivity and structural stability, several 25 mole% lanthanide-doped $Bi_2O_3$'s were investigated. At this dopant concentration there is a one-to-one correspondence between the number of dopant cations and vacant anion sites. The rate of conductivity decay at 500 °C varies dramatically and systematically with dopant, Fig. 1. As the radius of the dopant cation becomes smaller, the rate of the conductivity degradation becomes faster. The least rate of degradation is that of 25DySB, which has the largest cation radius and resultant lattice parameter, while the fastest rate is that of

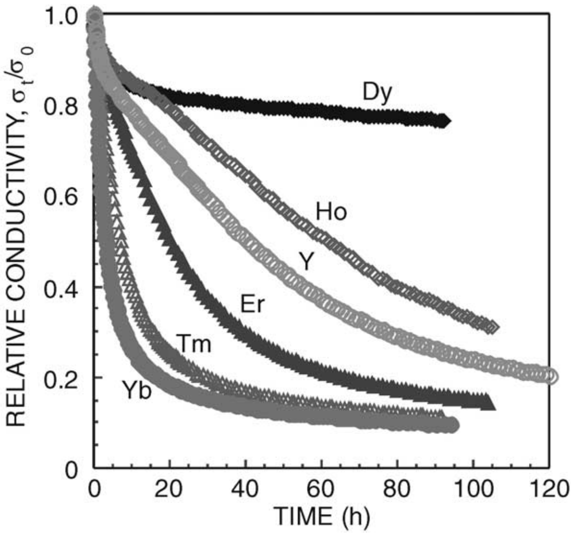

Fig. 1. Relative conductivity decay at 500 °C (from ref. 10).

25YbSB, which has the smallest cation radius and resultant lattice parameter.

The time dependence of the conductivity decay can be represented by an empirical equation:

$$\sigma(t) = \sigma(\infty) + [\sigma(0) - \sigma(\infty)]\exp\left[-(t/\tau)^{\beta}\right] \tag{1}$$

where σ(0) is the initial conductivity, σ(∞) is the conductivity at infinite time, τ is a pertinent time constant, and β is a dimensionless parameter. The longer the time constant the more stable (at least kinetically) is the structure. The time constants of these fcc-stabilized $Bi_2O_3$ samples were calculated[10] and are plotted in Fig. 2 as a function of cation radii and lattice parameter. As can be seen in Fig. 2, the logarithm of the time constant increases linearly with both increasing cation radii and lattice parameter for the different dopants.

The conductivity decay was also investigated as a function of dopant ($Er_2O_3$) concentration at 500 °C.[10] $Er^{+3}$ is smaller than that of $Bi^{+3}$, thus the lattice parameter decreased linearly with increasing dopant concentration. However, in contrast to the data in Fig. 2 the time constant decreased linearly with increasing lattice parameter. Therefore, the independent variables in the structural-stability of cubic bismuth oxide are the dopant radius and concentration.

The polarizability of lanthanides increases linearly with radii,[20] thus the time constant should be linearly related to dopant polarizability. We confirmed this experimentally, thus indicating that large/highly polarizable dopants provide the greatest stability of the disordered structure in cubic bismuth oxide.[16]

## 3. Ordered and disordered structures

From the above studies we showed that the ordered structure consisted of both "occupational ordering" and "positional ordering". The occupational ordering can be described by alignment of vacant 8c anion sites in <111> directions, resulting in the TEM observed 2a×2a×2a superstructure.[12] The alignment of anion vacancies along <111> directions in the ordered structure of cubic $Bi_2O_3$ is consistent with the theoretical results for stabilized zirconia.[7]

The positional ordering consisted of displacement of the occupied anion sites in a <111> direction from the 8c to 32f sites, as observed by neutron diffraction.[15] Both of these types of ordering were required to obtain a structure factor consistent with experimental results. The resultant ordered structure is shown in Fig. 3.

The disordered structure was similarly investigated, and can be described by a simple fluorite structure (single unit cell) where the anion sites are statistically occupied by 3/4 oxygen ion (no occupational ordering). The disordered structure does have, however, some positional ordering.

## 4. Effect of structure on conductivity

Through the investigations of the ordered and disordered structures we determined the position and occupancy of each anion site in lanthanide "stabilized" cubic bismuth oxide. From this we calculated the dependence of jump distance ($\lambda = [0.866 \times 8c_{occupancy} +$

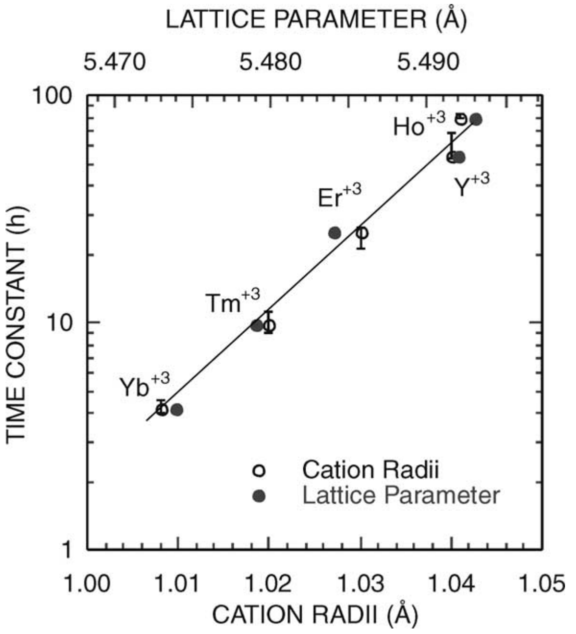

Fig. 2. Time constant as a function of dopant cation radii and resultant lattice parameter in 25MSB (from ref. 10).

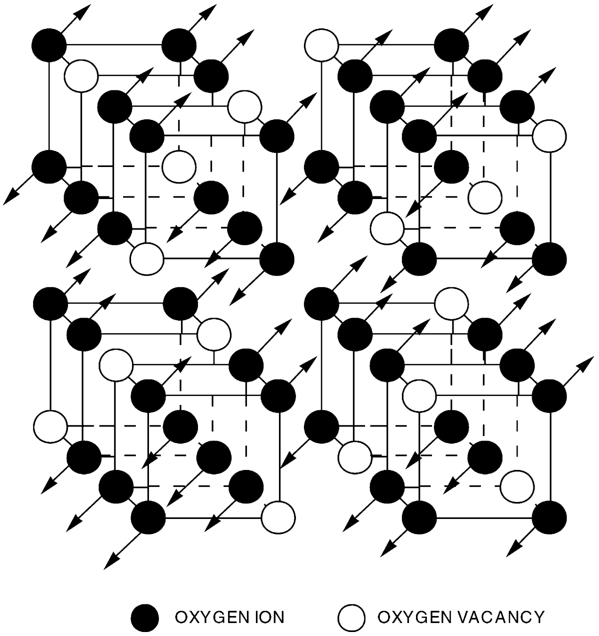

Fig. 3. Model of ordered structure showing both occupancy ordering (filled vs. vacant 8c sites) and positional ordering (<111> displacement toward 32f sites).

$0.693x32f_{occupancy}]a/3)$ on structure as well as available jump directions ($n=6$ for disordered and 1 for ordered structure), charge ($ze=1.5e$ for disordered structure and 2e for ordered structure) and concentration of mobile anions in a jump allowed position ($c_i=1$ for disordered and 0.333 for ordered structure).[17] With this information we calculated the conductivity pre-exponential factor (A) for the ordered and disordered structures.

$$A = n\lambda^2(ze)^2\nu c_i/6Vk \quad (2)$$

where ν is the pre-exponential of the jump frequency, V is the volume of the unit cell (from diffraction results for each composition) and k is Boltzman's constant. The decrease in jump distance due to positional ordering, and the decrease in available jump directions and concentration of mobile vacancies due to the combination of both types of ordering decreased the pre-exponential factor by an order of magnitude. These calculated results were in close agreement with experimental results. Further, these investigations showed that the decrease in pre-exponential factor overshadowed the effect of the decrease in activation energy upon ordering.

The influence of dopant radii and polarizability on structure dominated the pre-exponential factor and thus the conductivity, with larger more polarizable dopant cations providing a more stable disordered structure and resultant higher conductivity. To confirm this we synthesized a cubic $Bi_2O_3$ stabilized with two highly polarizable dopants, Dy and W.[18,19] The resultant DWSB has a conductivity twice that of ESB making it the highest conductivity phase stabilized fluorite oxide.[18,19]

## 5. Discussion and conclusions

There is a strong tendency for anions to order in <111> in highly defective fluorite oxides (anion vacancy concentrations $>\sim 10\%$). This has been reported for zirconia,[4–7] and as discussed here for bismuth oxide, and would appear to be a common feature for all fluorite oxides.

All of the lanthanide $M^{3+}$ dopants investigated have the same valence as $Bi^{3+}$ and a radii less than $Bi^{3+}$. Thus ordering of the anion lattice is due to differences in radii and polarizabilty, but not electrostatic differences between the host and dopant cations. As the radii increased toward that of $Bi^{3+}$ the disordered structure was more stable. Thus, there was a lower tendency to form an ordered anion lattice and/or vacancy associates.

Conversely, the closer the radii of the dopant is to the host cation the lower the tendency is to order the anion lattice. Ideally, then the dopant would have the same radii as the host. However, when the difference in radii is too small the fluorite structure cannot be stabilized down to room temperature.[10]

Finally, $Bi^{3+}$ is a highly polarizable cation due to its lone pair of electrons. As the radii of the lanthanide dopants was increased toward that of the $Bi^{3+}$ host cation the polarizability of these dopants also increased toward that of the $Bi^{3+}$ host cation. Thus, further investigation into the relative influence of radii vs polarizability is warranted.

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