Highlight Review

Defects and Conductivity in Ceria-based Oxides

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Abstract

The electrical conductivity of ceria solid solutions has been extensively investigated for many years, and many theories have been advanced to explain the differences seen in ostensibly identical materials. This short review looks at some recent theoretical and experimental evidence which has thrown new light onto the complex interplay between the cation and anion sublattice in these technologically important materials.

♦ Introduction

The defect chemistry of the fluorite oxides has been extensively studied over the last 50 years, particularly the binary solid solutions formed by zirconia, ceria, or thoria with the divalent alkaline earths and the trivalent rare earth oxides. These solid solutions are oxygen deficient, and oxygen vacancies charge-compensate the lower valent solute cations. Zirconia only adopts the fluorite structure (at moderate temperatures) when the solute concentration is large, because the small size of the Zr^{4+} cation (0.84 Å in eight-fold coordination) is not large enough to stabilize the fluorite structure to low temperatures. In contrast, pure ceria and thoria adopt the fluorite structure as, for example, the Ce^{4+} cation (0.97 Å in eight fold coordination) is large enough to be stable in the fluorite structure. The oxygen vacancies are mobile at elevated temperatures, hence the materials are excellent oxygen ion conductors and have many applications as electrolytes in sensors, solid oxide fuel cells, and oxygen separation devices. An example of the charge compensation that occurs upon solution of the lower valent oxide is given below for yttria addition to ceria to form material with the general formula $Ce_{1-x}Y_xO_{2-x/2}$.

$$Y_2O_3 \xrightarrow{CeO_2} 2Y'_{Ce} + 3O_O^x + V_O^{\bullet\bullet} \qquad (1)$$

The oxygen transport in the solid solutions is easily characterised by the measurement of the electrical conductivity as most of the materials have transport numbers for oxygen very close to 1. A major feature seen in all conductivity data for all these materials is the maximum in the isothermal conductivity of these oxides with respect to the content of the aliovalent solute. A maximum is to be expected when the oxygen sublattice is half occupied,[1] but it is generally found to happen at much lower solute contents, in the region of $x \approx 0.07$.

The ionic conductivity of any material is given by an Arrhenius type expression

$$\sigma T = \sigma_0 \exp\left(\frac{-E_a}{RT}\right) \qquad (2)$$

Where R is the gas constant, and T the absolute temperature. Two parameters directly govern the conductivity, σ, the pre-exponential factor, σ_o, and the activation energy for conductivity, E_a. In this short review we shall concentrate on the activation energy, as low activation energies sustain high conductivities to low temperatures, a current goal for SOFC development, but it must be remembered that the pre-exponential also has a marked effect upon the level of the conductivity. The activation energy consists of two parts, the enthalpy of migration, ΔH_m, for the oxygen vacancy and any terms caused by the interaction of the vacancy with other point defects. For dilute solutions of the trivalent cation the interaction term is thought to be due to the formation of defect associates, or dimers, of the oxygen vacancy with the solute cation, of the type shown below for ceria–yttria.

$$Y'_{Ce} + V_O^{\bullet\bullet} \rightleftharpoons (Y'_{Ce}V_O^{\bullet\bullet})^{\bullet} \quad \Delta H_a \qquad (3)$$

The equation above shows the simple associated defect pair, but note that the concentration of solute cations is double that of the oxygen vacancies they produce. This means there is a high probability of forming larger clusters as the solute concentration increases, a point which we will discuss later. If only simple associated pairs were to form, then E_a would be given by the sum of $\Delta H_a + \Delta H_m$.

An important point to remember is that when associates form the oxygen vacancy concentration can be defined in two ways. The normal definition is the stoichiometric vacancy concentration, which is that determined by the solute concentration through the electroneutrality condition; however, for transport measurements we must consider the mobile or "free" vacancy concentration, resulting from the equilibrium above, which of course can be very different, depending upon the magnitude of ΔH_a. Only these "free" vacancies are mobile and can contribute to oxygen ion transport in these solid solutions.

♦ Ceria-based Materials

For the next part of the review we shall concentrate almost exclusively on ceria solid solutions and experimental studies of the oxygen ion conductivity in these materials. What has been known for some time is that at solute concentrations close to the maximum in the isothermal conductivity there is a minimum in E_a. In a very detailed study of solid solutions of ceria with the trivalent rare earths, Faber et al.[2] showed that the minimum, and the concentration at which it occurs, depends upon the nature of the rare earth solute. The activation energy data are shown in Figure 1.

Wang et al.[3] explained the minima by the interplay of competitive defect interactions. At solute concentrations below

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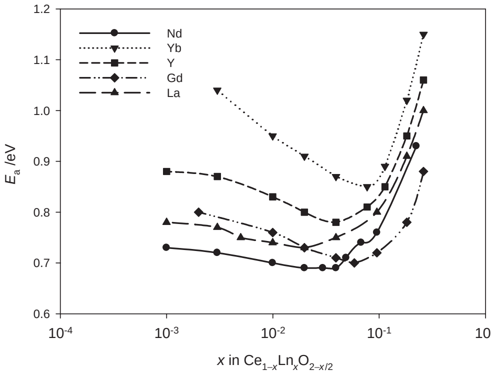

Figure 1. Activation energy vs. concentration for ceria solid solutions. Data from ref 2.

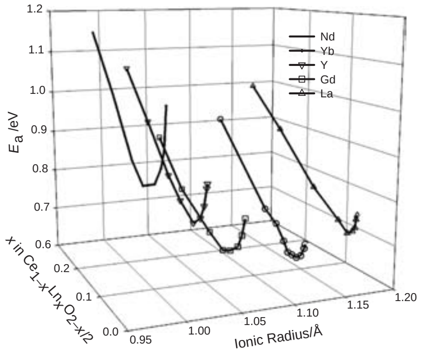

Figure 2. Activation energy of ceria solid solutions vs. concentration and ionic radius. Data from ref 2.

≈1%, there is a weakening of the association energy caused by an electrostatic interaction between the associated pair and the unassociated solute cations, which have opposite effective charges in the lattice. At solute concentrations greater than the minimum, larger clusters can form, which act as deeper traps for the oxygen vacancies and thus increase the total activation energy.

Inspection of Figure 1 shows there are differences between the compositional dependence of the activation energy for each of the solute species. This is apparent for both the shape of the dependence and the depth of the minimum, which is remarkable because the solute cations have the same effective charge in the fluorite lattice and give rise to identical stoichiometric vacancy concentrations. When these same data are plotted in three dimensions, by including the ionic radii of the solute cation, as in Figure 2, it is clear that there is a further minimum here as a function of the size of the solute ion. In Figure 3 the minimum of the activation energy found for each solute is plotted as a function of the ionic radius of the solute ion. Figure 2 is a three-dimensional plot, and there is a global minimum giving the lowest total activation energy for ceria solid solutions, which is dependent upon both solute size and concentration. At present the data only roughly map out this activation energy surface, and later we will discuss ways in which the plots might be extended to cover regions where no suitable ion exists. We have assumed that, to a first approximation, the migration enthalpy in these solid solutions is roughly constant and that the observed changes in E_a reflect changes in the association energy. If this is the case then Figures 2 and 3 demonstrate that the association energy must contain two terms. One Coulombic term that reflects the electrostatic attraction between the components (and which should be independent of solute type) and an elastic term representing the size mismatch of the solute with the host lattice.

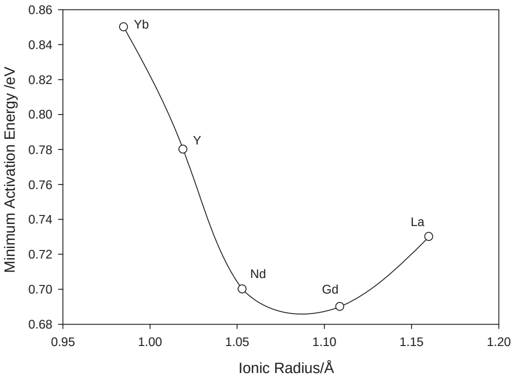

Figure 3. The minimum activation energy for each ceria solid solution plotted against ionic radius of the solute.

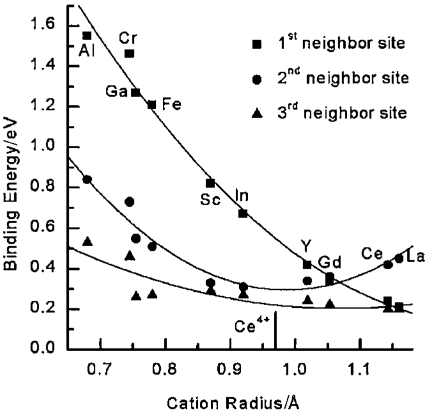

Figure 4. Calculated binding energies of vacancy solute pairs in ceria vs. ionic radius of the trivalent solute. The ionic radius of the host cation, Ce^{4+} is shown for comparison from ref 4.

Lattice Simulations

Early calculations sought to explain the minimum in activation energy with ion size (at $\approx Gd^{3+}$) in terms of the size mismatch and the elastic component of the association energy of the simple pairs (see early references in Ref. 1). More recent and sophisticated atomistic simulations by Minervini et al.[4] showed that the situation is much more complicated and that, in fact, the minimum is caused by the switch over of the configuration of the associated pair in the fluorite lattice, from the vacancy being a near neighbor to the solute ion for $r_{ion} \leq Gd^{3+}$, to second nearest neighbour $r_{ion} \geq Gd^{3+}$, as the solute size exceeds that of the host, as shown in Figure 4.

Zacate et al.[5] found a similar size dependence for zirconia solid solutions and additionally showed that the same type of size dependence could be found for larger clusters of vacancies and solute cations. Very recent density functional theory calcu-

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lations for ceria have confirmed this solute size trend[6] and have shown that at solute sizes where the crossover takes place, the energy difference for the vacancy between first and second neighbor sites is minimal, because of a balancing between the electrostatic and elastic interactions.

Most of the calculations, mentioned above, are consistent in their account of the size dependence; however, this explanation seems to be incomplete. Recent calometric studies by Navrotsky et al.[7] have shown that in CeO_2–Y_2O_3 and CeO_2–Gd_2O_3, the oxygen vacancy is, as expected, a first nearest neighbor, but the same was thought to be true for their work on CeO_2–La_2O_3 solid solutions in which the solute ions are above the size where a crossover to second neighbor should take place. It is possible that many other factors still need to be taken into account in the analysis of this type of data.

◆ Clustering

It is clear from Figure 1 that for these solid solutions the defect structure has a strong apparent concentration dependence. For meaningful comparisons between different solutes it is thus necessary to compare identical materials. However the concentration dependence of the activation energy (Figure 1) is different for each solute cation, thus comparison at equivalent concentrations may not be valid. Andersson et al.[6] show that the balance between the electronic and elastic component of the pair-binding energy, depends upon the solute type. Thus the type of clustering of defects is expected to be dependent upon both the concentration and type of solute used. We should also expect that around the minimum activation energy for each case, a change in the defect structure takes place.

To investigate this we need to examine evidence from using localized probes, as conductivity simply gives an averaged view of oxygen transport. The synchrotron-based EXAFS and XANES can look at the local coordination of the cations in these solid solutions,[8,9] and electron beam-based techniques such as EELS and SAED[10] yield further structural and chemical information. Most of these techniques have been applied to materials with solute concentrations much greater than 0.05 where clusters larger than dimers are to be expected. Even in these more concentrated solid solutions, the different trivalent solutes show differing cluster structure. Yamazaki et al.[8] studied ceria–yttia and ceria–gadolinia using EXAFS and XANES. They conclude that ceria–yttria is more likely to form large defect clusters than ceria–gadolinia, with the most probable clusters being two or four trivalent cations together with one or two oxygen vacancies, in near neighbor configurations. Deguchi et al.[9] reached the same conclusion when they studied the same solid solutions plus ceria–lanthana. Again they report that the tendency to cluster is strongest for ceria–yttria. They also suggested that the radial distribution functions for the solute ions (e.g. R(Ln–Ln)) and those found in the corresponding lanthanide sesquioxides are very similar concluding: "*it is interesting to note that the original structure of each dopant oxide is kept even in the ceria lattice*." This theme is continued by recent work by Ou et al.,[10] who use electron beam techniques on the ceria–samaria, –gadolinia, –dysprosia, and –ytterbia systems. The defect structure is shown to change with concentration, albeit for materials with high solute concentrations ($x = 0.15$ and 0.25). They propose that ordered nanodomains exist, essentially large defect clusters that resemble the parent C-type rare earth structure of the solute oxide. In contrast to Deguchi et al.,[9] they determine that the tendency of the system to cluster follows the order (Gd, Sm) > Dy > Yb. Somewhat at odds with the synchrotron-based techniques.

◆ Double Doping

One question that arises from the previous analysis is what is the optimum substitutional ion to provide the minimum association enthalpy and thus provide the maximum conductivity at low temperatures, assuming the optimum solute concentration can be achieved? This question is one which several people have attempted to answer.

In an early paper on the subject Kilner[11] suggested that one way to follow the changes that occur upon substitution is to follow the lattice parameter as a function of the concentration of the substituting cation. The concept was to minimize the disturbance to the ceria lattice, and hence the elastic trapping of the oxygen vacancies would also be minimized. In a later paper this idea was developed by Kim.[12] who suggested the concept of a value of a critical radius for the cation, r_c, which neither expanded or contracted the host fluorite lattice and suggested that for ceria this value is 0.1038 nm, close to that for Gd^{3+}.

Andersson et al.[6] have recently attempted to answer this question in a much more sophisticated manner in their DFT calculations. As mentioned earlier they suggest that at the minimum in the association (binding) energy where the crossover takes place, there is a balance between the electrostatic and elastic interactions that removes the energy difference between first and second neighbor configurations. They conclude that the optimum substitutional would lie between the atomic numbers 61 (Pm^{3+}) and 63 (Sm^{3+}) and suggest (from calculations) that double substitution with either Nd and Sm or Pr and Gd might provide an optimised solution, as Pm is radioactive.

The idea of using double doping is not a new idea. Ralph et al.[13] used double doping in an attempts to achieve optimum bulk conductivity in doped cerias using La/Yb and Sm/Y couples keeping the total trivalent substitution level at 0.06. The idea was to vary the "effective" or "average" ionic radius of the solute cations by mixtures of large and small cations. However, they found that by comparison with a material singly substituted by Gd at the same total concentration the singly substituted material showed the highest bulk conductivity. Their conclusion was that Gd provided the lowest local strain within the lattice and that in the other cases the oxygen vacancies became trapped at the sites of the smaller of the two solutes implying that these strain effects are very local to these cations. This finding was similar to those of Li et al.[14] who studied Sc^{3+}- and Gd^{3+}-doped ceria by EXAFS and found that oxygen vacancies bind tightly to the smaller Sc substitutionals. It should be noted that these two studies have used cations with a rather large difference in ionic radius, e.g., Sc^{3+} and Gd^{3+} and that in all cases one of the cations has a substantial size difference to the host Ce^{4+}. In this case the lattice distortion caused by the large ionic radius mismatch of this ion may indeed dominate.

The situation appears to be different when the suggestion made by Andersson et al.[6] is taken up, and the two codoping cat-

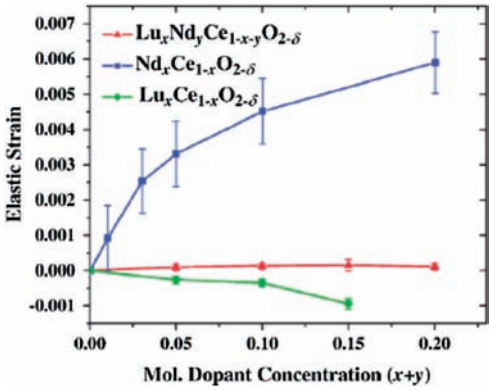

Figure 5. Lattice elastic strain as a function of solute content, from ref 17.

ions are close to the size of the host. Several recent papers have reported improvements in the ionic conductivity[15–17] of ceria when doubly doped. Of particular interest is the work of Omar and co-workers. In their first paper[17] they studied cerias cosubstituted with Lu/Nd, following similar ideas to those used by Ralph et al.[13] to try to verify the r_c concept forwarded by Kim.[12] As an indicator of the elastic strain in the lattice they used the fractional change in lattice parameters vs. total substitution content to show that by adding the correct proportions of Lu^{3+} and Nd^{3+} they produced an effectively unstrained ceria lattice. Their data is shown below in Figure 5 together with the data from Stephens and Kilner.[18]

It is clear that the cosubstitution of Nd and Lu has a minimal effect upon the lattice parameter of the ceria. The conductivity of the codoped material was higher than either for the singly Lu- or Nd-substituted material, but did not manage to better the lattice conductivity of the equivalent Gd-substituted samples. In a second publication, and following the publication by Andersson et al.,[6] Omar et al.[16] have used the suggested Sm/Nd substitution, at a level of 0.1 to obtain material that showed a higher conductivity than the corresponding singly substituted Gd analogue, with a small reduction in activation energy. Interestingly the lattice parameter of this material increases linearly with substitution, unlike the quadratic variation found by Stephens and Kilner[18] who studied singly substituted Nd (data shown in Figure 5). The quadratic behavior is a strong deviation from the expected linear Vegard's law and is indicative of strong defect interactions. It would seem that from the improved conductivity data it is beneficial to reduce these strong defect interactions, but is not clear why double substitution should achieve this and is clearly worthy of further investigation.

♦ Conclusion

Although this is a much studied area, as pointed out in the introduction, it is surprising that so much new information has come to light recently. Of particular note is the use of a combination of experiment and theoretical calculations to elucidate the complex defect behavior observed, however, much remains to be understood. We lack a formalism to describe the complex defect structures that undoubtedly form at the highest substitutional levels. We also need to fully understand the complex interplay between the distribution of host and substitutional species on the cation sublattice and how this affects the observed oxygen transport behavior in these fascinating complex and important materials.

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