# Defect Chemistry of Proton Incorporation in Bulk and Grain Boundary Structures of $ZrO_2$ and YSZ

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$ZrO_2$-based materials are well known for their high oxide ion conductivity and for their various technological applications including solid oxide fuel cells (SOFCs). The introduction of $Y^{3+}$ to $ZrO_2$ stabilises the high temperature cubic polymorph and introduces charge compensating oxygen vacancies which produce the sought after high ionic conductivity in the system. In addition to oxygen ion conductivity, interest in proton conduction in both the bulk and grain boundary structures of $ZrO_2$-based materials has also increased in recent years [1]. Recent studies have shown that proton transport can occur at temperatures lower than 150 °C and that this transport is driven by the grain boundary structures in the material [2]. There is ongoing debate as to whether protonic conduction occurs primarily in the grain boundaries, the bulk or the inner surfaces of YSZ. It is the aim of this study to determine the energetics of proton incorporation as well as the redox properties of undoped $ZrO_2$ and YSZ to assess the consequences for proton conduction.

In this work we use the lattice statics simulations whereby ions are treated as charged spheres and the short-range forces are accounted for by the interatomic potentials and the long-range ionic interactions are treated using Coulombic terms. We have used the $ZrO_2$ potential model developed by Woodley *et al*. [3] as it has the best agreement with experimental parameters [4]. All defect energies are calculated using the Mott-Littleton method [5]. An attractive Morse potential is used to model the O-H interaction [6]. All calculations were completed using the general utility lattice program (GULP) [7].

We have calculated proton incorporation energies/hydration energies for both bulk $ZrO_2$ and YSZ with a variety of Y concentrations. In addition, both the $\Sigma 5(210)/[001]$ and $\Sigma 5(310)/[001]$ grain boundaries (Figure 1) in these materials have been considered. Calculations confirm dramatically lower proton incorporation energies in and around the grain boundary. For the YSZ grain boundaries the difference is even more significant with energies 3-4 eV lower than the respective values for the bulk material. The vast majority of calculated are positive, but only the energies for the YSZ grain boundaries are ‘close to zero’ as reported by experiment [8]. The energies of reduction are also shown to be significantly reduced at the grain boundary structures, although no significant reduction in the oxidation energies is observed. Comparison of the bulk and grain boundary structures of both $ZrO_2$ and YSZ show that the introduction of Y to the fluorite structure significantly reduces the hydration energy. Our calculations also show that protons prefer to reside in the vicinity of Y ions (Figure 2), an observation confirmed by previous calculations [9]. In future calculations we will assess the effect of Y segregation in the YSZ grain boundaries on the hydration energies.

In summary, this study represents one of the first true computational assessments of protons in bulk and grain boundary structures of $ZrO_2$ and YSZ. Our results clearly suggest a far higher concentration of protons in the grain boundaries compared to the bulk. This conclusion supports the argument that proton conduction primarily occurs in the grain boundaries of YSZ.

References

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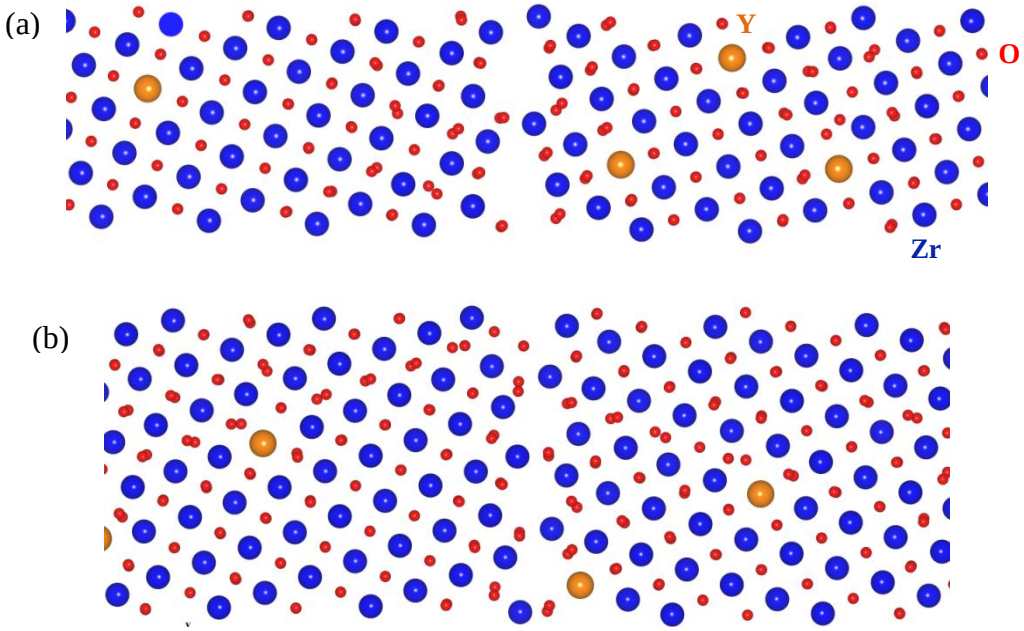


Fig. 1: Example configurations for the (a) $\Sigma 5(210)/[001]$ and (b) $\Sigma 5(310)/[001]$ grain boundaries in 3.5 mol% YSZ.

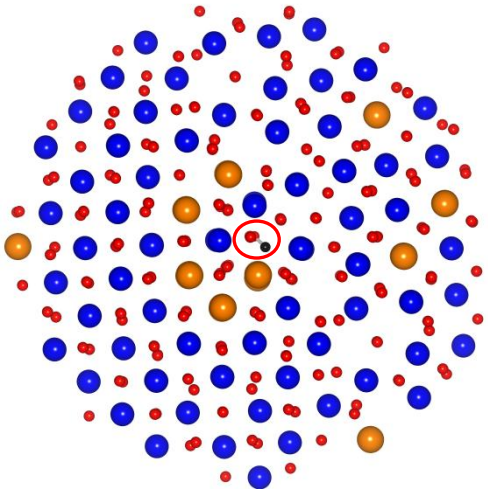

Fig. 2: Schematic of the lowest energy configuration for a proton-doped 14 mol% YSZ $\Sigma 5(310)/[001]$ grain boundary.