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Oxygen Transport and Association in Yttria Stabilised Zirconia

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1. Introduction

Zirconia is widely used due to its high oxygen diffusivity in various technological applications like gas sensors, fuel cells, catalytic membranes etc. The material shows an excellent thermal stability, combined with very good mechanical properties.

Adding lower-valent cations to zirconia leads to the formation to a high concentration of oxygen vacancies on the anion sublattice. The stabiliser ions, typically Y^{3+} or Ca^{2+}, are generally distributed randomly on the cation sublattice. In contrast, the distribution of the oxygen vacancies is known to be non-random, but the exact structure of the anion sublattice is still not well known.

It is the goal of this paper to investigate the anion sublattice in zirconia stabilised with yttria as a function of stabilised content using static lattice calculations. In particular, the method of supercells was applied in order to get the mean association enthalpy for reality-like systems.

The simulation results can be compared to experimental values of activation enthalpies for anion diffusion and anion conductivity obtained previously.

2. Computer simulation

Perfect lattice calculations were performed using the program GULP [1]. Supercells [2] with different concentrations of yttria (3 to 55 mol%) were setup by randomly placing both cations and oxygen vacancies on an initially perfect cubic ZrO_2 lattice. Each supercell consists of 256 ZrO_2 units. Parameters for Buckingham potentials were chosen from the literature [3]. For each concentration, at least ten supercells were created, and the results of the ten independent calculations were averaged.

After performing an energy minimisation run, the lattice energy was obtained and compared to results of previous defect calculations [3]. Other parameters, in particular the lattice constants, and bulk properties like modulus were also checked to agree with the known experimental values.

3. Results and discussion

During the simulation runs, the position of the oxygen ions were not constant, but they were shifted to other, better positions. Initially, in the perfect random structure, the lattice energy was much more scattering than after the lattice optimisation. The lattice energy was compared to the perfect lattice energy using the following equation:

$$E_{assoc}(x) = \{E_{latt}(x) - E_{latt}(x=0) - x \bullet (E(V_O^{2\bullet}) + 2 \bullet E(Y_{Zr}'))\} / x$$

x is the number of oxygen vacancies in the supercell, $E_{latt}(x)$ is the lattice energy at the defect concentration x, and $E(V_O^{2\bullet})$ and $E(Y_{Zr}')$ are the energies for creating one isolated respective defect in perfect ZrO_2, taken from [3]. The resulting energy difference, taken as E_{assoc}, is plotted as a function of the yttrium content in Fig. 1.

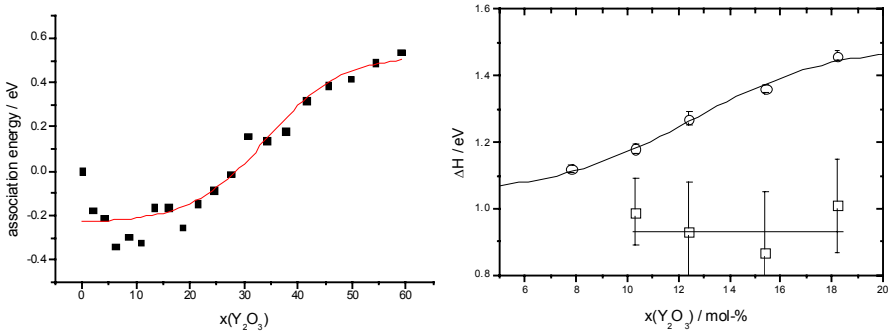

Fig. 1: Calculated association energy E_{assoc} (left) and experimental activation enthalpies ΔH (right; circles: conductivity, $\Delta H_{\sigma T}$; squares: self-diffusion, ΔH_O; [4]) in YSZ.

In this plot, also experimental results on tracer diffusion and low-temperature conductivity are included [4]. The shape of the concentration-dependency of the association energy E_{assoc} and $\Delta H_{\sigma T}$ are very similar: Both are increasing with increasing yttria content. Even more, the absolute values of the increase are comparable; they are about 0.6 eV (calculated) or 0.4 eV (experimental). Subtracting the calculated E_{assoc} from $\Delta H_{\sigma T}$ leads to a constant enthalpy of 0.8 eV. Other investigations on the oxygen transport in YSZ gave values between 0.3 and 0.7 eV for the pure transport [5]. Our value is slightly higher, confirming that the migration is most relevant for oxygen transport. Association enthalpies are increasing with yttria content, since non-associated oxygen vacancies, which are close to Zr^{4+}, do not find appropriate surroundings and have to react with Y^{3+}.

4. Conclusion

It is possible to calculate the vacancy association enthalpy in highly defective solids using perfect lattice methods. For YSZ, association enthalpies up to 0.6 eV were received, leading to an enthalpy of about 0.8 eV for the migration of an oxygen vacancy.

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