



Full length article

Structure and ionic diffusivity in an yttria-stabilised zirconia/strontium titanate multilayer

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ABSTRACT

Enhanced ionic conductivity observed in a heteroepitaxial multilayer of yttria-stabilised zirconia and (YSZ) and strontium titanate (STO) has variously been attributed to lattice dilation or a disordered oxygen sublattice, leading to high interfacial mobility of anions, as compared to those of the constituent bulk oxides. We seek to understand the mechanism of ionic motion in such heterostructures by first simulating the atomic structure assuming coherent interfaces. After investigating possible low-energy interface structures using a genetic algorithm, we perform molecular dynamics simulations on these structures to examine the anionic diffusivity in the system. We find that the extreme biaxial tensile strain in the YSZ layer, as imposed between layers of STO, induces phases that differ from fluorite. The lowest energy structure is an unknown phase, which we refer to as quasi-cubic and whose cation sublattice resembles an extension of the perovskite; this structure does not lead to enhanced ionic conductivity, in contradiction to some reports in the literature.

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1. Introduction

Pure ZrO₂, at ambient temperature and pressure, exists in the monoclinic (baddeleyite) phase, transforming to the tetragonal phase at 1440 K and then the cubic fluorite phase at 2640 K [1]. The formation of the latter phases are not restricted to high temperatures only, for these phases may be stabilised at lower temperatures by oxygen vacancies introduced into the lattice with aliovalent doping [2]. The vacancies, which compensate for the charge difference between the Zr⁴⁺ host ions and the aliovalent substituent ions, play another perhaps more important role in that they provide low energy paths for oxygen ion migration through the lattice via vacancy hopping. Yttria-stabilised zirconia (YSZ) is one such oxygen ion conductor, whose oxygen ion mobility at elevated temperatures is sufficiently high for industrial applications such as an electrolyte in high temperature solid oxide fuel cells (SOFC) [3,4].

However, its ionic conductivity at lower temperatures leaves much to be desired [5]. A popular approach to address this

limitation in recent years has been to manipulate the dimensions of its lattice such that the energy barrier for vacancy hopping is reduced [6,7]. This effect has been demonstrated only theoretically at extreme compression of the lattice [8], but has been realized experimentally for lattices under expansive strain. By growing very thin oxide films epitaxially on carefully selected single crystal substrates, so that the interface is coherent or semi-coherent, the oxide lattice can be forced to alter its dimensions to accommodate the underlying lattice of the substrate material. For YSZ films deposited onto substrates such as Lu₂O₃, Y₂O₃, MgO and Gd₂Zr₂O₇, which impose modest biaxial tensile strains of up to 3% on the YSZ lattice, the ionic conductivity of the films increase by up to two orders of magnitude in comparison with the same material in the bulk [9–11]. Replacing the substrate material with (001) SrTiO₃ (STO) would result in a tensile strain of 7% in the (001) YSZ lattice, supposing a perfectly coherent interface between the substrate and the film; such a heterostructure of a 1 nm-thick YSZ layer sandwiched between layers of STO reportedly achieves eight orders of magnitude enhancement in conductivity, which, it was suggested, is due to greatly increased ionic mobility at the highly strained interfacial planes [12].

If the main contribution to the measured conductivity is indeed ionic, such a dramatic improvement is unprecedented. Electronic

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conductivity is more likely to attain this magnitude, and could arise from unintentional p-type doping of the STO substrate [13–16]. The fact that the YSZ/STO interface is observed to be atomically sharp and completely coherent is equally unexpected, as the enormous amount of strain is more likely to have been relieved by dislocations which may possibly contribute to enhanced ionic conductivity [17]. An attempt to reproduce the result [18] revealed that the orientation and growth mode of the deposited YSZ film depends on the termination plane of the (001) STO substrate. When a SrO plane terminates the substrate, the YSZ film grows epitaxially with (001) orientation, whereas a TiO₂-terminated substrate results in island growth of tilted (111) YSZ. Another study [19] finds a dependence of the YSZ film orientation on the growth rate: slow deposition rates yield highly coherent (001) films on TiO₂-terminated STO but higher deposition rates at the same growth temperature produce incoherent islands of (110) YSZ that are partially connected. The conductivity of these films are then found to correlate with the epitaxial quality of the films, with the former having high conductivity but that of the latter comparable to a bare STO substrate. In contrast, a YSZ/STO multilayer, fabricated using a different method in another investigation [20], exhibits enhanced conductivity of similar magnitude to that of the coherent STO/YSZ_(1nm)/STO trilayer [12], although in this case the YSZ layer is discontinuous and formed of YSZ islands with both (001) and (110) orientations. Nonetheless, the increased conductivity in this specimen is not of anionic origin, as the authors observed no diffusion of isotopes in their ¹⁸O tracer experiments.

As reports on the conductivity measurements of the YSZ/STO system are contradictory, theoretical studies seek to understand the origin of the observed enhancement, if any. Since tensile strain of the lattice has been shown to result in an increase in ionic conductivity, these theoretical works examine whether extreme expansion of bulk YSZ lattice could produce massively enhanced ionic mobility. In almost all of these works, the YSZ lattice is assumed to be fluorite. Several investigations on anionic diffusivity in ZrO₂ as a function of biaxial strain revealed an optimum strain at 3% and 4% using classical and density functional theory (DFT) calculations respectively, with an improvement in the diffusivity of at most four orders of magnitude [21–23]. While these results are unable to explain the high conductivity observed experimentally, the authors of these papers, as well as those of several other works, make an interesting observation. Above the optimum strain, local geometry optimisation of the strained fluorite lattice produces a structural transformation. In two of these works, the authors note a change in coordination of the ions [21,22]. In Refs. [23–26], the authors show their resulting structures in which the coordination of the Zr⁴⁺ ion with the O²⁻ ions is sixfold instead of eightfold as in the fluorite phase, strongly resembling the columbite (α -PbO₂) phase. In agreement with these results, a study on the stability of various theoretical structures of ZrO₂ with strain, finds several phases more stable than the fluorite phase at high values of strain, most of which consist of Zr⁴⁺ ions in sixfold coordination. One of the most stable of these is the columbite phase [27].

Pennycook et al. find, using simulated annealing with DFT, yet another phase of ZrO₂ that transforms from 7%-strained cubic fluorite lattice [28]. They describe the oxygen sublattice as being arranged in a ‘zigzag’ manner when the lattice is projected onto the (001) plane. When YSZ is layered with STO, they find a disordered oxygen sublattice from their simulations and also observe sublattice disorder from elemental maps of oxygen with electron energy loss spectroscopy (EELS) [29]. Performing *ab initio* molecular dynamics (MD) simulations on bulk pure ZrO₂ with the zigzagged oxygen sublattice, including a vacant oxygen site, they estimated at 500 K a 4×10^6 enhancement in the ionic conductivity of this structure relative to that of the unstrained stabilised fluorite phase

in the bulk. However, their reported simulated times, which were up to 6 ps, were too short for a straightforward application to the unstrained lattice of the Einstein relation, which is the linear relationship between the mean squared displacement and the diffusion coefficient. The diffusion processes at low temperatures are too slow to calculate a mean squared displacement over a few picoseconds. So to obtain an estimate of the ionic diffusivity for the unstrained lattice at a low temperature, these authors performed a single simulation at 2500 K, which they combined with the experimental Arrhenius barrier (1.1 eV) for bulk YSZ from Ref. [12] to extract an estimate of the pre-exponential coefficient in an Arrhenius formula. With this formula they then extrapolated their 2500 K diffusion coefficient down to 500 K. The error introduced by this procedure is difficult to estimate, but we believe it might be significant – see section 3.2 below.

Clearly, the straining of the ZrO₂ lattice alone is not able to produce eight orders of magnitude enhancement in the ionic conductivity of the YSZ/STO system, even when accompanied by a change in the structure. However, the investigations of ZrO₂ lattice strains have largely neglected the effect of yttrium dopants, whose interactions with oxygen vacancies have been shown to significantly affect ionic conduction in ZrO₂-based materials [30–36]. Furthermore, the effect of STO when layered with YSZ, on the diffusivity of oxygen ions in the multilayer has not been reported and so the mechanism for ionic diffusion in the system has not yet been examined. We therefore present in this report our investigation of coherent YSZ/STO structures and calculations of oxygen ion diffusivities in the system. As the strained bulk ZrO₂ studies mentioned above suggest strongly the need to consider phase changes in highly strained states, we probe the phase space using a hybrid strategy to seek low energy structures. Classical interatomic potentials, being cheap to compute, are first used in conjunction with a genetic algorithm to obtain a set of plausible structures. Since these potentials are poor at predicting energies with better than qualitative accuracy, we then perform DFT calculations to further relax the geometries in order to obtain a more reliable ordering and magnitude of the energies. We find a stable YSZ phase with both SrO and TiO₂-terminated STO layers, whose cation sublattice resembles those of perovskite as well as fluorite but whose oxygen ion sublattice is different from those of oxides that we are aware of. This phase is further stabilised by intermixing between the YSZ and STO layers. MD simulations that we perform on these multilayer structures suggest a mechanism for oxygen ion diffusion within the YSZ layers; however, our calculated diffusivities and activation energies of the oxygen ions indicate no enhancement of ionic conductivities, but rather a reduction in the oxygen ion mobility as compared to that in bulk YSZ.

2. Computational details

We construct three configurations of YSZ/STO multilayers in periodic supercells with interfacial areas that are equivalent to 2×2 unit cells of STO. When we make the STO layer 2.5 unit cells thick, the termination planes on either side of the layer are both SrO planes or TiO₂ planes; we consider these two cases and refer to the supercells as having SrO interfaces and TiO₂ interfaces respectively. In the third supercell with interfaces that we label as “mixed interfaces”, the STO layer is 2 unit cells thick and thus is terminated with a SrO plane on one side and a TiO₂ plane on the other. In each of our supercells we strain 1.5 unit cells thick of fluorite ZrO₂ layer on the STO layer in the orientation suggested by Garcia-Barriocanal et al.: the [001] direction of the fluorite lattice is parallel to the [001] direction of the perovskite lattice but rotated 45° about [001], i.e. $[110](001)_{\text{YSZ}} \parallel [100](001)_{\text{STO}}$ [12]. To introduce 8 mol% of Y₂O₃ doping in the ZrO₂ layer, two Y³⁺ ions replace two randomly

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