Origin of Colossal Ionic Conductivity in Oxide Multilayers: Interface Induced Sublattice Disorder

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Oxide ionic conductors typically operate at high temperatures, which limits their usefulness. Colossal room-temperature ionic conductivity was recently discovered in multilayers of yttria-stabilized zirconia (YSZ) and $SrTiO_3$. Here we report density-functional calculations that trace the origin of the effect to a combination of lattice-mismatch strain and O-sublattice incompatibility. Strain alone in bulk YSZ enhances O mobility at high temperatures by inducing extreme O disorder. In multilayer structures, O-sublattice incompatibility causes the same extreme disorder at room temperature.

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The ability of solid-oxide fuel cells (SOFCs) to directly and cleanly convert chemical energy into electrical energy with high efficiency could play a major role in reducing carbon emissions and preventing climate change [1]. In a SOFC, oxygen is reduced to O ions at the cathode, transported though an electrically insulating electrolyte to the anode, where it combines with H to form water and electricity. The efficiency of this process is limited by the ability of the electrolyte to conduct O ions. Very high temperatures have so far been required to achieve sufficient O conductivity. Yttria-stabilized zirconia $(Y_2O_3)_x(ZrO2)_{1-x}$ (YSZ) is currently the most commonly used electrolyte, but requires temperatures of around 800 °C or more for useful levels of oxygen conductivity [1–4]. High temperatures require the use of potentially costly heat-resistant materials, reduce durability, and limit the number of possible applications for SOFCs. These constraints have motivated a search for novel alternative electrolytes capable of providing high oxygen conduction at low operating temperatures [1–4].

Two primary mechanisms have so far been invoked to account for large, so-called superionic conductivities. In the first case, there is a vacant sublattice that is unavailable to the mobile ion at low temperatures. As the temperature is increased, ions transfer randomly to the vacant sublattice and, at some critical temperature, an order-disorder phase transition sets in leading to a highly conducting disordered phase [5,6]. This mechanism is often referred to as ‘‘sublattice melting.’’ In the second case, ionic conduction is merely diffusion by the vacancy-mediated mechanism, i.e., vacancy hopping [6,7]. In the case of YSZ, instead of relying solely on temperature to produce vacancies, a supply of O vacancies results from replacing ZrO_2 units with Y_2O_3 units in the cubic-fluorite lattice. Other bulk materials with a built-in supply of O vacancies, such as $Ce_{1-x}M_xO_{2-\delta}$ (M: Sm Gd, Ca, Mn), have shown promise, exhibiting useful levels of O conduction at temperatures between 500 and 750 °C [1]. The most impressive improvements in ionic conductivity have been demonstrated in heterogeneous structures. Very recently, by placing YSZ containing 8 mol % yttria between layers of $SrTiO_3$ (STO), a colossal enhancement in the ionic conductivity of up to 8 orders of magnitude was observed near room temperature [8]. The conductivity of STO/YSZ/STO trilayers was found to be very large for thin YSZ layers that are strained an enormous 7% to match the STO lattice. The conductance exhibits virtually no dependence on the layer thickness, from which the authors inferred that colossal conduction occurs primarily in the near-interface region. The authors further noted that the YSZ and STO oxygen sublattices do not match at the interface, which is likely to result in either O vacancies or disorder in the interfacial plane, leading to increased conductivity. These features are indeed consistent with *superionic* conduction, but the origin of the observed *colossal* conductivity remained elusive. More recently, Guo has questioned the interpretation of the data in terms of colossal ionic conduction [9], suggesting that the observed conductivity enhancement is an electronic effect. The authors of [8] countered in support of the original interpretation [10].

In this Letter, we report density-functional calculations to investigate the order of magnitude of ionic conductivity that is possible in YSZ-STO multilayers. We found that colossal ionic conductivity can be explained in terms of a combination of lattice-mismatch strain and O-sublattice incompatibility as follows: Using finite-temperature dynamical simulations of bulk cubic zirconia with a built-in supply of O vacancies, we found that 7% strain completely changes the O sublattice. At high temperatures the oxygen structure becomes extremely disordered, so much so that by 2000 K the O sublattice appears completely random. At these high temperatures, the mean-square-displacement (MSD), and therefore the mobility, of the O atoms in the strained structure are greatly enhanced over the already superionic unstrained structure. The enhancement correlates with the degree of O disorder, but is not mediated by sublattice melting as no enhancement is observed without vacancies. The key to understanding the *low-temperature* colossal ionic conductivity lies in the finding that the incompatibility of the oxygen sublattices at the YSZ-STO interface, together with the 7% lattice-mismatch strain, cause an *extreme* O-sublattice disorder at room temperature that is comparable to the disorder found in strained bulk vacancy-doped zirconia at 2000 K. We can, therefore, using the high-temperature data estimate the low-temperature conductivity of the strained multilayers to be 10^6 times higher than in unstrained bulk zirconia. Sata *et al.* [11] have reported up to 2 orders of magnitude enhancement in the ionic conductivity by space-charge effects in thin multilayers, which suggests that space charge may produce the extra 2 orders of magnitude seen experimentally. Finally, the present calculations provide an answer to the puzzle of the stability of the YSZ epitaxial films with 7% strain to thicknesses of up to 30 nm in an apparent serious violation of lattice-mismatch theory [12]. We found that a new phase exists with an optimum strain of 5.2%.

The calculations, including finite-temperature quantum molecular dynamics (MD) [13] were performed using density-functional theory [14,15] in the generalized-gradient approximation and the projector-augmented-wave method [16] with a plane-wave basis as implemented in the Vienna *ab initio* simulation package (VASP) code [17]. Supercells containing two unit layers of zirconia and three unit layers of STO were used for the multilayer calculations. The zirconia was expanded 7% such that the cation lattices fit together perfectly. The experimental STO layer is sufficiently thick that the middle atomic planes are not affected by the interfaces. As we cannot include as many STO atomic planes in the calculations, we freeze the positions of the atoms in the middle plane, allowing the rest of the planes to relax. Although this may force the STO to take on its bulk structure more quickly than in reality, it provides the necessary feature of preventing the interfaces from affecting each other through the STO. The height of the multilayer supercell was then varied using an in-plane width of one unit cell. The structures were relaxed with an energy cutoff of 343 eV and up to a $6 \times 6 \times 6$ Monkhorst-Pack k-point mesh centered at the Γ point.

The energetically optimum height was then used as the starting point for finite-temperature MD simulations. As the colossal ionic-conductivity of the multilayers is observed in-plane, we used supercells made of three unit cells in the two lateral directions and two units cells high for bulk MD simulations. For the larger multilayer calculations we used supercells two unit cells by two unit cells wide, again with two and three unit layers of zirconia and STO, respectively. MD calculations were performed using only the Γ point in k space, with an energy cutoff of 250 eV. Atomic motion time-steps of 3.6 fs were used so that no atom could travel further than 0.1 Å per time-step [18]. Bulk 0 K relaxations of single zirconia unit cells were performed using an energy cutoff of 250 eV and $8 \times 8 \times 8$ k-point meshes.

We first investigated the effect of the 7% expansive strain using simulated annealing for bulk cubic ZrO_2 from 2000 K to 0 K. In Fig. 1 we show snapshots of the strained structure at three temperatures and compare them with the structure of unstrained cubic ZrO_2 at 2000 K. It is evident that 7% strain results in a completely new O sublattice. At temperatures of 1000 K and below the O atoms are organized into zigzags. The zigzags are more complicated than the simple alternating O displacements seen in tetragonal zirconia. Furthermore, the O atoms in the strained zigzag phase are in 7-fold coordination around the cations, as in amorphous ZrO_2 [19]. At higher temperatures, the O atoms are increasingly disordered until by 2000 K the zigzags have completely disappeared and the O sublattice appears amorphous. This result contrasts sharply with the unstrained structure in which even at 2000 K most of the O atoms display only Debye-Waller type oscillations about the cubic-fluorite tetrahedral positions (Fig. 1).

The mobility of the O atoms was studied by calculating their thermal MSD as a function of time in MD calculations for up to 6 picoseconds (Fig. 2). Without any vacancies, no net displacement occurs. Even with one vacancy per supercell at 2000 K, the superionic unstrained zirconia still produces no MSD on this time scale. Applying 7% strain to the zirconia with a single vacancy, however, we find that significant O MSD occurs as low as 1000 K. As no

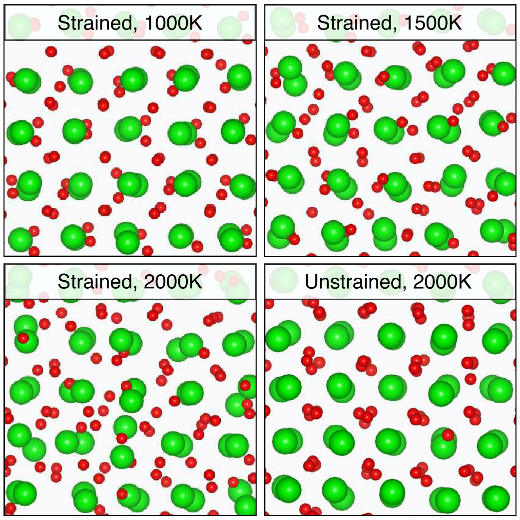
Strained, 1000K
Strained, 1500K
Strained, 2000K
Unstrained, 2000K

FIG. 1 (color online). Zirconia structures resulting from quantum mechanical simulated annealing at various temperatures. O atoms are shown as small red spheres, and Zr atoms in green. The 7% expansive strain is in the plane of the page. The zigzag ordering of the strained O sublattice shown at 1000 K persists down to 0 K, but begins to break down at higher temperatures. At 2000 K and above the O positions appear random, in contrast to the unstrained material in which most O atoms simply oscillate about the cubic-fluorite positions.

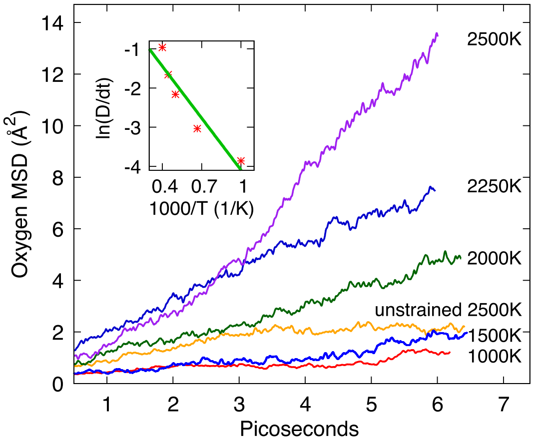

FIG. 2 (color online). MSD of O atoms as a function of time during MD simulations at various temperatures. (Inset) Arrhenius plot of D from the strained MSDs (Å^2/ps). The linear fit shown in green yields an energy barrier of 0.4 ± 0.1 eV.

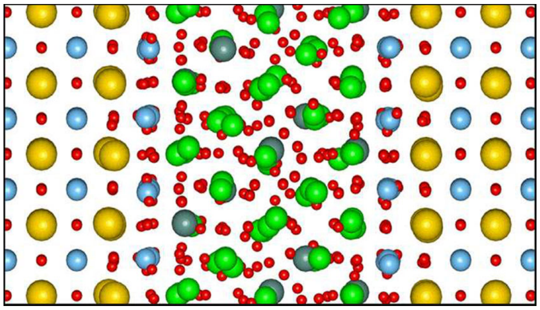

FIG. 3 (color online). Structure of the 1 nm YSZ layer sandwiched between layers of STO at 360 K. Sr atoms are shown as large yellow balls, Ti in blue, Zr in green, Y in gray, and O in red.

motion occurs without vacancies, the mobility is not mediated by "sublattice melting" but by vacancy hopping.

With vacancies, the strained zirconia O MSD increases with temperature and correlates with the degree of disorder. At 1000 and 1500 K, where a degree of zigzag ordering remains, plateaus occur in the MSD corresponding to periods of time without hopping. At 2000 K and above, where the O sublattice appears random, the MSD increases continuously. The activation barrier extracted from an Arrhenius plot of the diffusivities (Fig. 2 inset) is 0.4 ± 0.1 eV, smaller than the 0.6 eV reported by [8].

To investigate the role of the interface, we determined the structure down to 360 K by performing simulated annealing of the STO-YSZ multilayers starting from 1200 K, which is roughly the substrate temperature used during growth of the multilayers in the experiment. The result is shown in Fig. 3. Unlike in the bulk strained zirconia, the O sublattice near the interface remains highly disordered all the way down to 360 K. In fact, the multilayer YSZ O sublattice appears to have the same degree of disorder at 360 K as the strained bulk at 2000 K. The presence of the interface therefore causes the high-temperature phase with its very low hopping barrier to persist down to low temperatures.

We now estimate the enhancement of the ionic conductivity in the multilayers over that of bulk YSZ. Using the Einstein relation $\langle r^2 \rangle = 6Dt$ we obtain diffusivities from the MSDs. We can then solve for the preexponential D_0 in the expression for the diffusivity, $D = D_0 \exp(E_b/kT)$, in which E_b is the energy barrier, k is the Boltzmann constant, and T is the temperature. The value of D can then be extrapolated to low temperatures. The Nernst-Einstein relation, $\sigma = Nq^2D/kT$, in which q and N are the charge and density of the mobile ions, can then be used to obtain conductivities from diffusivities.

It is not feasible to obtain a reliable estimate of the absolute value of the conductivity of O vacancies because of a large uncertainty in the density and the fact that the charge on the ions is ill-defined. We can, however, estimate the effective magnitude by evaluating the ratio of the conductivity in the strained disordered phase to that in the unstrained phase $\sigma_s/\sigma_b = D_s/D_b$, assuming the density and charge of the carriers to be the same in both phases. For the strained phase preexponential, we use the average of the preexponentials determined at each temperature a MSD was calculated. As previously noted, the unstrained phase was not conductive enough to show any net motion even at 2000 K. By increasing the temperature to 2500 K, however, we were able to get a single MSD slope for the unstrained phase. As an energy barrier cannot be obtained from a single temperature, we used the 1.1 eV experimental energy barrier for the unstrained bulk material [8] in the expression for D_b. Using this method, we estimate the ionic conductivity of the strained disordered phase to be 4×10^6 times higher than that of unstrained bulk YSZ at 500 K, close to the 8 orders of magnitude reported experimentally.

It is evident that the disorder induced by the strain and the presence of the interface are responsible for the majority of the observed colossal enhancement in ionic conductivity. In halide based multilayers such as BaF_2/CaF_2, space-charge effects enhance ionic conduction up to about 2 orders of magnitude for thin layers [11]. Our estimate for the conductivity enhancement in the thin YSZ multilayers does not include space-charge effects, so it may well be that space-charge effects provide the last 2 orders of magnitude enhancement.

The results of the simulations also allow us to gain further insights into the cause of the extreme O-sublattice disorder in the YSZ layer of the multilayer structure. The O sublattice of bulk zirconia under 7% strain exhibits essentially the same zigzag ordering as shown at 1000 K in Fig. 1 all the way down to 0 K. It is this zigzag-ordered sublattice that is juxtaposed with the STO O sublattice. The zigzag ordered YSZ O atoms occupy sites that are close to tetrahedral positions. On the other hand, O atoms in STO occupy octahedral positions. Evidently, the incompatibility of the STO and YSZ O sublattices is causing the observed O disorder. Figure 3 shows that at 360 K there are relatively small O-atom displacements on the STO side of the interface. In contrast, because the YSZ is strained by 7%, the O sublattice is more flexible and succumbs to the perturbation, exhibiting extreme disorder. The stable STO structure controls the positions of the O atoms in the YSZ interfacial plane, forcing them all to occupy octahedral positions. This constraint then disturbs the O atoms in the underlying layers of YSZ, with no Ti neighbors, that are free to disorder.

We probed the above issue further by examining the energetics of O vacancies at the YSZ interfacial plane. When one of the octahedral O atoms in the YSZ interfacial plane is removed and the structure relaxed, an O atom from further into the YSZ immediately moves to fill the octahedral vacancy. This preference for full occupation of the octahedral O positions at the interfacial plane is consistent with electron energy-loss spectra reported in [8] which shows no difference between the Ti oxidation state at the interface and deep within the STO. As long as there are O atoms occupying all the octahedral positions in the interfacial plane, the effect of the STO seems to only be felt through the displacement of neighboring O atoms. When vacancies are placed in positions away from the interfacial plane the vacancies do not relax to another layer. These results indicate that vacancy hopping, and therefore ionic conduction, occurs preferentially in a region adjacent to the interfacial plane, where the O atoms are perturbed but unconstrained by the STO.

It is natural to infer that the extreme disorder seen at 360 K in the thin 1 nm YSZ O sublattice tapers off with distance from the interface in thicker layers of YSZ. Colossal conductivity, therefore, is likely to occur only in a relatively thin section of the YSZ layer adjacent to the interface. This thin disordered section would completely dominate the conductivity, resulting in the lack of variation in the conductance with YSZ thickness observed experimentally for 1–30 nm YSZ layers [8].

Increasing the YSZ layer thickness to 62 nm causes a three-orders-of-magnitude drop in the ionic conductivity, which was attributed to relaxation due to exceeding the critical thickness of the YSZ [8]. Lattice-mismatch theory for epitaxial films, however, suggests that for 7% mismatch strain, the critical thickness ought to be extremely small [12], not on the scale of tens of nanometers. The present calculations resolve this quandary. The zigzag structure resulting from simulated annealing in the strained bulk represents a new zirconia phase that becomes energetically favorable at high strains. Varying the in-plane strain of the zigzag structure results in a parabolic dependence of the total energies centered around 5% strain. The total energy of the 5% strained zigzag structure is only about 0.16 eV per unit cell higher than the total energy of the unstrained cubic-fluorite structure. At 7% strain, the total energy of the zigzag structure is 0.49 eV higher, but this is still 2.76 eV lower than the cubic-fluorite structure strained to the same dimensions. The phase change, therefore, reduces the energy penalty imposed by the strain, and allows the YSZ layer to remain coherently strained up to 30 nm. Once the strain is released the present calculations suggest that the ionic conductivity would drop significantly, as observed.

In conclusion, we have used first-principles calculations to demonstrate that the origin of the observed colossal ionic conduction in STO-YSZ-STO structures is a combination of strain on the YSZ and extreme disordering of its O sublattice, with both phenomena caused by *lattice-constant* and *structure* mismatch between the two materials. We also showed that the misfit strain is sustained because YSZ exhibits a stable phase with large strain.

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