New insights into the origin of the oxide ionic diffusion change in strained lattices of yttria stabilized zirconia

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ABSTRACT

The effect of the lattice strain on the oxygen diffusion is currently under discussion since it could lead to major enhancements of the ionic conductivity. In this work, this effect has been analyzed by using molecular dynamics simulations for yttria stabilized zirconia. The oxygen mass transport properties have been studied and analyzed for compressive and tensile strains in a wide range of temperatures between 859 K and 1959 K. A continuous enhancement of the diffusivity has been observed for moderate strains ($\varepsilon < 4\%$), especially at low temperatures. A maximum of two orders of magnitude can be extrapolated at 400 K. The origin of this enhancement lies in the reduction of the vacancy migration barrier through the Zr–Zr jump environment. Although the migration barrier even approaches zero at $\varepsilon \sim 3\%$, a limitation of further enhancement by lattice strain is observed due to an almost constant relaxation enthalpy ($\Delta H_r \sim 0.36$–0.40 eV). For high values of lattice tensile strain (above 4%), a dramatic drop in the oxygen diffusion properties occur. The origin of this behavior is based on the strong distortion of the cationic sublattice and the formation of new equilibrium positions for the oxygen along the diffusion pathways (both contributing to increase the relaxation enthalpy up to values as high as $\Delta H_r > 0.89$ eV). This disordered structure reduces the oxide ion mobility, even below the one of the relaxed lattice. An exceptional case corresponds to the formation of new lattice structures by strain lattice relaxations. In this work, the relaxation of one of the highly strained lattices leads to the formation of an interface with enhanced oxide ionic diffusivity. This type (or similar) fast ionic conduction interfaces are proposed to be in the origin of recently reported ionic conductivities significantly above the expected enhancement due to elastic strains.

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1. Introduction

Recent studies [1,2] have shown a big potential of ionic conductors in the form of thin films and nanocrystalline structures, pointing out the drastic impact of interfaces and size effects on ionic conduction and mass storage. The most striking example is the recently published colossal ionic conduction at interfaces of yttria-stabilized zirconia (YSZ)/strontium titanate (STO) epitaxial heterostructures where a coherent interface is maintained even for extremely high lattice strains (above 7% in YSZ) [3]. Although, in this case, the charge carrier could not be confirmed to be the oxygen above 540 K [4–7], the indications from this and other similar works [8–12] suggest that a substantial enhancement could exist due to interfacial effects, particularly at low temperatures.

These surface or interface effects originate from changes of the charge carrier concentration or mobility attributed to local fields arising from lattice strain [13,14], dopant segregation [15,16] or

the presence of a high density of lattice defects (dislocations, stacking faults, macles) [9]; or the formation of space-charge layers [1,17]. Although excellent works have been recently published shedding some light on the ionic conduction phenomena at the nanoscale [18], experimental studies, usually based on thin films, intrinsically convolute several of these relevant contributions, yielding ambiguous (and controversial) interpretations. Moreover, the analysis of the origin/effects of these phenomena at an atomic level is always a challenge since only few experimental techniques can be employed to study the local environments at the elevated temperatures required for activating the ionic conductivity. Besides the high structural complexity, due to the presence of static defects at low temperatures, the ionic motion itself induces a disorder in the structure. The inherent dynamic nature of this disorder prevents from using time- and volume-averaged studies (Bragg diffraction from X-ray or neutron diffraction) only allowing difficult-to-interpret techniques such as diffuse scattering [19,20], EXAFS spectroscopy [21–23], conductivity relaxation measurements [24,25], nuclear magnetic resonance (NMR) spectroscopy [26,27], quasi-elastic light scattering [28], europium fluorescence

spectroscopy [29,30] or tracer diffusion experiments [31,32]. Due to the difficulty in understanding these phenomena on the basis of experimental data, computer modeling has become a popular way to study the ionic conduction from an atomic level point of view.

In particular, different atomic scale simulation studies have recently been published dealing with the effect of the lattice strain on the oxygen diffusion in yttria stabilized zirconia [33–38]. Araki and Arai [33] reported molecular dynamics (MD) simulations of YSZ under various stress conditions, suggesting that oxygen diffusion could be enhanced by applying directional stresses. Kushima and Yildiz [34] combined density functional theory (DFT) with kinetic Monte Carlo (KMC) to conclude that a maximum in oxygen diffusion is expected at around 4% of tensile strain with more than three orders of magnitude of enhancement at 400 K. By employing classical molecular dynamics, independent works of Dezanneau et al. [35] and Tarancón et al. [36] confirmed the presence of an increased diffusivity with an optimal value of biaxial lattice strain ca. 3%. Finally, Pennycook et al. [37] performed finite-temperature quantum molecular dynamics by DFT of YSZ thin films sandwiched between two rigid STO layers obtaining enhancements of 6 orders of magnitude at 500 K. According to Pennycook et al., the origin of this great enhancement corresponds to a combination of elastic and plastic deformations that generate a new YSZ phase with an extremely disordered oxygen sublattice (especially close to the STO interface).

In this paper, results from classical MD simulations of strained YSZ lattices ($\varepsilon = -3\%$ to 7.2%) in a wide range of temperatures (859–1959 K) are presented. Apart from revisiting and complementing the limits of the conductivity enhancement previously published [34–37], this work provides a comprehensive explanation of the origin of the change in diffusivity in strained lattices from an atomistic point of view. Therefore, after analyzing the averaged static/dynamic properties such as radial distribution functions (rdf), mean square displacement (msd) or ionic distances, a previously presented methodology [15] is used to analyze the evolution of the charge carrier motion at an atomic scale, i.e. vacancy migration pathways, conduction model for vacancies and energy landscapes. Special attention is devoted to tensile strains above 4% since they induce extremely disordered structures that, eventually, generate new interfaces with enhanced ionic diffusivity.

2. Methods

2.1. Molecular dynamics simulations

Molecular dynamics simulations on closed isothermal systems in isochoric (N,V,T) or isobaric (N,P,T) conditions have been carried out on relaxed and strained 8 mol% Y_2O_3-doped ZrO_2. The MOLDY package has been employed [39]. The predictor–corrector Beeman algorithm was used for integrating the equations of motion. The interaction between ions was introduced via a Born–Mayer–Buckingham potential for short range interactions, supplemented with electrostatic terms for long-range ones,

$$V(r_{ij}) = -\frac{C}{r^6} + A\exp\left(-r/\rho\right) \qquad (1)$$

The parameters A, ρ and C were obtained from the literature [40]. For the cation–cation interactions, only Coulomb forces were assumed. The Ewald sum technique was used to handle long range electrostatic forces. The cutoff parameters for the real and reciprocal spaces were automatically calculated via the Fincham's analysis for reducing the CPU time. This kind of description does not consider polarization effects of the ions due to induced dipoles. However, although the rigid-ion model employed here cannot fully

describe the dynamics of the system like the shell model employed in previous works [34], it can provide qualitative and quantitative information about the structural and dynamical properties of ionic conductors consuming a reasonable computational time [41].

A cubic simulation cell consisting on $5 \times 5 \times 5$ crystallographic unit cells was generated. After location of Zr^{4+} and O^{2-} in their regular lattice site (cationic cubic fcc with fully oxygen occupation of tetrahedral sites), a random substitution of Zr^{4+} by Y^{3+} was performed to achieve the desired composition. The dopant pattern has been randomly generated but kept fixed for all the temperatures and configurations. One oxygen vacancy was introduced every two dopant ions. The periodic boundary conditions were imposed using the link cell method.

Constant (N,P,T) simulations were performed to determine the associated unit cell volumes for the relaxed configuration at each temperature. In constant-pressure simulations the cell size and shape change in response to the imbalance between the internal and the external applied pressure. The values obtained for the unit cell parameters were in good agreement with the literature showing less than 0.4% difference for the whole range of temperatures under study (see Ref. [15]). The dynamics of the unit cell matrix is governed by the so-called Parrinello–Rahman Lagrangian controlled by an inertial fictitious mass that was chosen $W = 50$. An isotropic modification of this method has been used in these first simulations.

After volume determination, classical (N,V,T) simulations were performed. Three different parts have been separated in every simulation: velocity scaling (40,000 time steps, each of 2 fs of duration), equilibration (10,000 time steps) and production (250,000–850,000 time steps). The initial Maxwell–Boltzmann distribution of velocities was re-scaled by a factor s every 200 time steps to the desired temperature,

$$s = \sqrt{\frac{gk_BT}{2K}} \qquad (2)$$

where g is the number of degrees of freedom, T the temperature and K the kinetic energy.

Accurate application of scaling implies the use of an average kinetic energy at the denominator of s, but, at equilibrium, the kinetic energy of the system fluctuates. To solve this problem, a kinetic energy coming from an average over the previous 175 steps was used for the re-scaling of particle velocities. For each run, the variation in total energy was not larger than 0.0003% and the temperature varied <1.5%. The temperature range covered in this work goes from 859 K to 1959 K.

Different types of strain were imposed by fixing the volume of the cells in the (N,V,T) MD simulations. Isotropic compressive (negative) and tensile (positive) strain was applied to the original lattice. The range of strain covered in this work goes from −3% to 7.2%.

2.2. Data analysis: averaged static properties

Static structure of matter can be measured by the radial distribution function $g(r)$, which describes the spatial organization of molecules around a central molecule [42]. Specifically, it is proportional to the probability of finding two atoms separated by a distance $r \pm \Delta r$. Since molecular dynamics provides positions of individual atoms as functions of time, $g(r)$ can be readily computed from molecular dynamics trajectories.

The radial distribution function for homogeneous substances is defined by,

$$g(r) = \frac{1}{N\rho}\left\langle \sum_{i}^{N}\sum_{j\neq i}^{N}\delta[r - r_{ij}] \right\rangle \qquad (3)$$