ChemComm

Hop, skip or jump? Proton transport in the $CaZrO_3$ perovskite oxide

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Received (in Cambridge, UK) 29th January 2001, Accepted 2nd March 2001
First published as an Advance Article on the web 19th March 2001

***Ab initio* simulations of the $CaZrO_3$ proton conductor predict that the transport mechanism involves proton transfer between adjacent oxygen ions (but predominantly inter-octahedra), and that the energetics of proton–dopant binding is favourable in accord with spectroscopic evidence.**

Metal oxides with the ABO_3 perovskite structure have received considerable attention as solid-state proton conductors,[1,2] with a range of promising electrochemical applications including fuel cells, gas sensors and hydrogen pumps. Most attention has focused on cerates[3] and zirconates[4] which possess varying levels of proton conductivity. An important example is the development of a potentiometric sensor for hydrogen in molten metal based upon doped $CaZrO_3$ as the proton-conducting electrolyte.[5] The $CaZrO_3$ material is typically acceptor-doped with trivalent ions (*e.g.* In^{3+}) at the Zr^{4+} site, which is crucial to proton dissolution.

It is acknowledged that the macroscopic behaviour of materials is often controlled by fundamental mechanisms acting on the microscopic scale. However, the information derived from most conductivity experiments is not sufficient to identify the precise mechanistic features of proton transport. There is also conflicting debate as to whether there is any significant interaction between the dopant ion and the protonic defect (hydroxyl ion at oxygen site), which may lead to defect clustering or proton 'trapping'.

In an attempt to gain further insight into these problems we have investigated the important $CaZrO_3$ material using quantum mechanical techniques based upon density functional theory (DFT), which are increasingly powerful tools for exploring solid-state properties. This preliminary account builds upon our previous atomistic modelling and X-ray absorption (EXAFS) studies, where we have already obtained valuable microscopic information on the defect chemistry of perovskite-type oxides.[6,7] Here we focus, for the first time, on the distorted orthorhombic phase of $CaZrO_3$, which extends earlier simulation work on ideal cubic perovskites.[8]

The present account of the computational techniques will be brief since more detailed reviews are given elsewhere.[9,10] The calculations are performed within the DFT framework, with the exchange-correlation energy being treated using the generalised-gradient approximation. The particular implementation of DFT employed here combines a plane-wave basis set with the total energy pseudopotential method (as embodied in the CASTEP code[9]) which is ideally suited to calculations on periodic systems. Our simulations are based upon ultrasoft pseudopotentials with the Brillouin zone sampled according to the Monkhorst–Pack scheme.[11] The DFT-pseudopotential approach can be utilised to perform *ab initio* dynamics which essentially combines the solution of the electronic structure with classical molecular dynamics (MD) for the nuclei. The MD simulations, which are highly computationally demanding, used a periodically repeated system of $Ca_4Zr_4O_{12}H$, a time-step of 0.5 fs and a total duration of 4000 time-steps at a temperature of 1000 K within the NVT ensemble; full computational details will be reported in ref. 12. It is worth noting that *ab initio* techniques of this kind have been applied successfully to other oxides including studies of molecular absorption on surfaces[13] and lithium intercalation.[14]

Table 1 Calculated and experimental structural parameters of orthorhombic $CaZrO_3$

	Experimental[a]	Calculated
Unit cell parameters		
a/Å	5.5912	5.5895
b/Å	8.0171	8.0550
c/Å	5.7616	5.7667
Mean bond lengths and angles		
Zr–O (×6)/Å	2.0964	2.1052
Ca–O (×4)/Å	2.3817	2.3742
Ca–O (×4)/Å	2.7616	2.7680
Ca–O (×4)/Å	3.5101	3.5345
Zr–O(1)–Zr/°	145.76	143.46
Zr–O(2)–Zr/°	146.50	146.35

[a] Ref. 15.

The starting point for this study, prior to the introduction of the proton, was the simulation of the equilibrium bulk structure. The perovskite structure of $CaZrO_3$ is built upon a framework of corner-linked ZrO_6 octahedra with the calcium ion in a 12-coordinate site. The orthorhombic structure (space group *Pcnm*) exhibits significant tilting of the octahedra from the ideal cubic configuration.[15] The calculated and experimental lattice parameters, bond lengths and bond angles are listed in Table 1. Examination of the values shows good agreement between experimental and simulated structures, with $< 0.5\%$ deviation in the cell parameters and bond lengths. In addition, the appreciable tilting of the ZrO_6 octahedra (and the corresponding Zr–O–Zr bending) are correctly reproduced.

Of primary interest here is the information on the microscopic mechanism revealed by the MD calculations. Graphical analysis of the evolution of the system with time shows a number of proton 'hopping' events during the simulation run. Fig. 1 presents 'snapshots' of one of these proton hops between neighbouring oxygen ions of connecting octahedra, illustrating initial and barrier (transition) states. This confirms that proton conduction occurs *via* a simple transfer of a lone proton from one oxygen ion to the next (Grötthuss mechanism), with no evidence for the migration of hydroxyl ions ('vehicle' mechanism) on the present timescale.

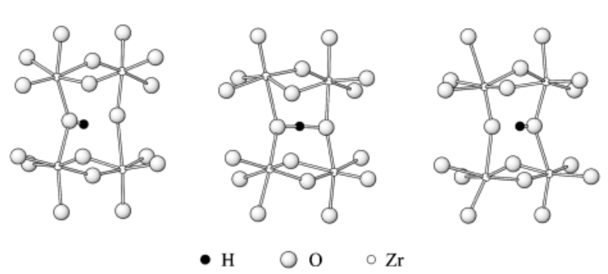

Fig. 1 Sequence of three snapshots from *ab initio* MD simulations showing inter-octahedra proton hopping in orthorhombic $CaZrO_3$ (the Ca ions are omitted for clarity).

DOI: 10.1039/b100960p

We also find rapid rotational and stretching motion of the O–H group, which allows the reorientation of the proton towards the next oxygen ion before the transfer process. However, the simulations reveal predominantly inter-octahedra proton hopping, rather than within octahedra. This diffusion path is influenced by the ZrO_6 tilting within the orthorhombic structure which leads to short oxygen–oxygen separations between the vertices of adjacent octahedra (shown in Fig. 1). These results are consistent with the observation that proton mobility is lower in perovskite structures deviating strongly from cubic.[1,2] There is also considerable lattice vibrational dynamics with large amplitudes of vibration of the oxygen ions. In particular, for each hopping event the O(H)–O distance shortens from equilibrium values (of *ca.* 2.7–2.9 Å) to < 2.4 Å so as to facilitate proton transfer; this suggests that migration is 'phonon-assisted'. We note that recent simulations of zeolites have found similar coupling between proton motion and framework dynamics.[16]

The interaction between oxygen ions and the proton is probed further by analysis of the electron density distribution (illustrated in Fig. 2 as a contour map for the inter-octahedra path). The barrier state displays a symmetric density distribution, in which there is equal hydrogen bonding to the two adjacent oxygen ions (leading to a shorter oxygen–oxygen distance). This confirms that the proton is not transferred through a totally 'free' state, so that all the OH bonds are never completely broken. Although additional analysis of the wavefunction would be useful, it is apparent that the host lattice exhibits localised spherical-like density about the nuclei indicative of the largely ionic character.

In an attempt to probe the question of proton–dopant association, we have undertaken a series of calculations on defect pairs $(OH_O^{\bullet}M'_{Zr})$ comprised of a hydroxyl ion and a neighbouring dopant substitutional; here we employed a slightly larger periodically-repeated system corresponding to $Ca_8Zr_7MO_{24}H$ in order to achieve a lower dopant content. Attention was focused on three commonly used dopants in $CaZrO_3$, namely Sc^{3+}, Ga^{3+} and In^{3+}. The binding energies were derived with respect to the two isolated defects where a negative value indicates the system is bound.

The resulting energies (reported in Table 2) predict that all the hydroxyl–dopant pairs are favourable configurations, with the lowest value for Ga^{3+}. Although there are no experimental data on $CaZrO_3$ for direct comparison, the calculated values are in accord with proton 'trapping' energies of *ca.* −0.2 and −0.4 eV for Sc-doped $SrZrO_3$ and Yb-doped $SrCeO_3$ respectively, derived from recent muon spin relaxation (μSR) and quasi-elastic neutron scattering (QENS) experiments.[17] These studies postulate that in the course of their diffusion, protons are temporarily trapped at single dopant ions. The present calculations therefore predict possible trapping effects and the presence of proton–dopant pairs in the $CaZrO_3$ material. It is noted, however, that defect pairs do not necessarily preclude the presence of isolated protons and dopant ions, since clusters will be in equilibrium with single defects. This picture can be viewed as analogous to oxygen ion conductivity in fluorite oxides and the well-known importance of dopant–vacancy interactions.[18]

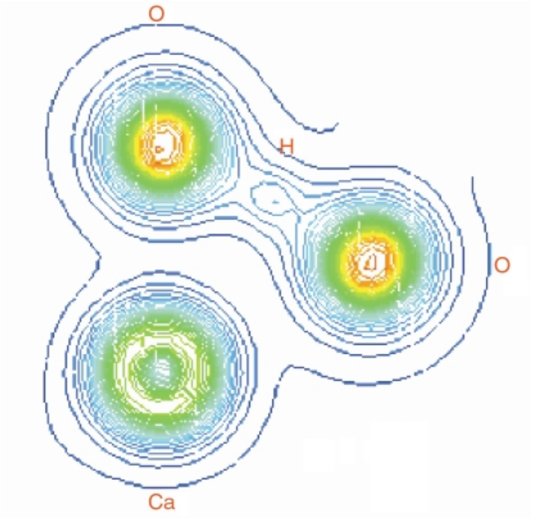

Fig. 2 Electronic charge density of the barrier (transition) state for inter-octahedra proton transfer in the plane defined by Ca, O and H (colour scale: high to low density is red to blue).

Table 2 Binding energies of hydroxyl–dopant pairs $(OH_O^{\bullet}M'_{Zr})$ at nearest-neighbour sites

Dopant	E_{bind}/eV[a]
Sc^{3+}	−0.31
Ga^{3+}	−0.18
In^{3+}	−0.30

[a] 1 eV ≡ 96.486 kJ mol^{-1}.

In summary, our *ab initio* simulation study has allowed us to gain significant insight as to the proton migration mechanism and proton–dopant binding in the $CaZrO_3$ orthorhombic perovskite at the microscopic level. This forms part of the continuing effort to improve our understanding of proton transport, a key phenomenon in a variety of systems that range from inorganic solids to biomolecules. Further simulation work is in progress and it is hoped that the present study prompts new experimental investigations in this area using, for example, neutron scattering or muon spin techniques.

We wish to thank the EPSRC for funding this work, the Royal Society for a University Research Fellowship (J. D. G.) and the Computational Chemistry Working Party for the use of the supercomputer facilities at the Rutherford Appleton Laboratory, UK.

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