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An apatite for fast oxide ion conduction†

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Atomistic simulations have allowed us to gain fresh insight into the mechanisms of oxygen ion transport in novel apatite silicates, which form part of a new family of ionic conductors for potential fuel cell applications.

Materials that exhibit good oxygen ion conductivity are of considerable interest for a range of "clean" electrochemical applications including solid oxide fuel cells and separation membranes. In this context, apatite oxides based on $M_{10}(SiO_4)_6O_{2\pm y}$ (where M = rare-earth, alkaline-earth) have recently attracted considerable attention following the report of higher ionic conductivities than the conventional yttria-stabilised zirconia electrolyte at moderate temperatures, opening up a new class of oxygen ion conductor.[1–6] More recently, conductivity and neutron diffraction studies[2] of lanthanum-based apatites report that the non-stoichiometric $La_{9.33}Si_6O_{26}$ system shows much higher conductivity and lower activation energy than the fully stoichiometric $La_8Sr_2Si_6O_{26}$ phase. It has been proposed that this is correlated with a degree of oxygen interstitial disorder in $La_{9.33}Si_6O_{26}$. In general, the cation-deficient (or oxygen-excess) materials are found to exhibit far higher conductivity than the stoichiometric compositions.[1–6]

Conduction in these materials has been shown to be wholly ionic, with high oxygen transference numbers ($>$ 0.9) across a wide range of oxygen partial pressures.[1] However, the information derived from most conductivity experiments is not sufficient to identify the precise mechanism of ion transport in these apatite oxides, and centres around conflicting debate between vacancy and interstitial migration. Such mechanistic detail on the micro- or nano-scale is crucial to a greater understanding of their macroscopic transport behaviour that underpins potential applications.

Atomistic modelling techniques are well suited to the investigation of such properties and have been applied successfully to studies of perovskite-type oxides,[7] aluminosilicates[8,9] and fluorapatites.[10] However, there is little previous work regarding the modelling of ion mobility in these new apatite oxygen ion conductors to link up with the experimental data. The purpose of this preliminary account is to report the use of such techniques to probe, for the first time, oxygen ion migration mechanisms in the model systems $La_{9.33}Si_6O_{26}$ and $La_8Sr_2Si_6O_{26}$.

The present description of these techniques will be brief since comprehensive reviews are given elsewhere.[11] The potentials describing the interatomic interactions are represented by pairwise potentials which include the long-range Coulomb term and an analytical function to model overlap repulsions and van der Waals forces. A well established three-body term for the angle-dependent SiO_4 tetrahedral units is also used. The transferability of this potential has proved successful in the modelling of a wide range of silicates and zeolites.[9,11] The shell model[12] provides a simple description of ionic polarisibility and has proved to be effective in simulating the dielectric and lattice dynamical properties of metal oxides. An important feature of these calculations is the modelling of lattice relaxation around the defect or migrating ion, which is treated by the Mott–Littleton approach (embodied in the GULP code[13]).

The apatite structure of these two phases exhibits hexagonal symmetry,[2] and consists of isolated SiO_4 tetrahedra with the remaining ions occupying channels running along the *c*-axis (Fig. 1). These complex apatites may be viewed as "hybrid" structures comprised of covalent-like [SiO_4] units and ionic-like M/O channels, which are not trivial to simulate. Prior to carrying out the defect calculations, energy minimisation of the perfect lattice is performed to generate an equilibrium structure based on our final set of potentials.[14] The calculated and experimental lattice parameters and mean bond lengths are listed in Table 1; these reveal good agreement between simulated and observed structures, thus supporting the validity of the potential model used for the subsequent defect calculations.

A series of simulations were first carried out on isolated point defects (vacancies and interstitials). Our calculated vacancy energies indicate that for both compositions an oxygen vacancy at the channel O5 position is the most favourable by over 1.5 eV. This is in accord with previous speculation that defect conduction is associated with the O5 oxide channels. We similarly find that the most favourable La vacancy is at La1/La2 by over 3 eV, which supports experimental models that find partial occupancy at these sites in cation-deficient $La_{9.33}Si_6O_{26}$. Powder diffraction experiments[2] suggest that oxygen interstitials occupy sites within the O5 channel, although accurate refinement has been difficult. Our calculations suggest that the lowest energy interstitial position (termed O7) lies at the periphery of the *c*-axis channel at *ca.* (0.013, 0.233, 0.876) for $La_{9.33}Si_6O_{26}$ in the P-3 space group. Analysis of the local structure indicates considerable distortion of the nearby SiO_4 tetrahedral unit. This result suggests the need for further structural work to examine such oxygen defect sites, although we recognise that diffraction analysis of such local distortions will be difficult.

Of primary interest here is information on the microscopic mechanism of ion transport. Atomistic simulations have carried out an extensive search of the potential energy surface for

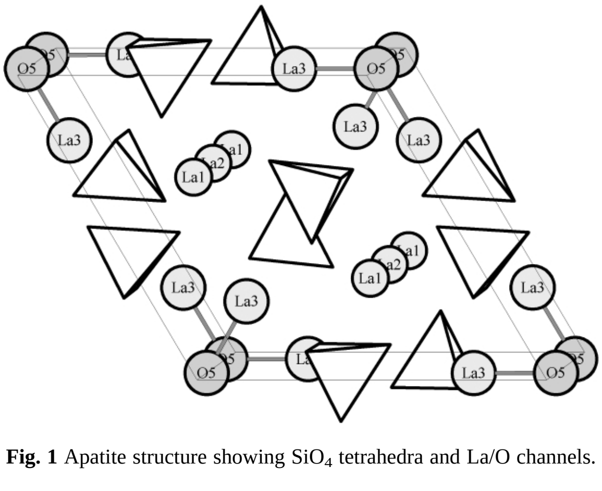

Fig. 1 Apatite structure showing SiO_4 tetrahedra and La/O channels.

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† Electronic supplementary information (ESI) available: interatomic potentials. See http://www.rsc.org/suppdata/cc/b3/b301179h/

Table 1 Calculated and experimental[2] structural parameters for $La_8Sr_2Si_6O_{26}$ and $La_{9.33}Si_6O_{26}$

(a) Lattice constants

	Experimental		Calculated	
Composition	*a*,*b*/Å	*c*/Å	*a*,*b*/Å	*c*/Å
$La_8Sr_2Si_6O_{26}$	9.7083	7.2377	9.8053	7.1558
$La_{9.33}Si_6O_{26}$	9.7248	7.1895	9.7607	7.1198

(b) Mean bond lengths

	$La_8Sr_2Si_6O_{26}$		$La_{9.33}Si_6O_{26}$	
Bond	Experimental/ Å	Calculated/ Å	Experimental/ Å	Calculated/ Å
Si–O	1.6267	1.6280	1.6231	1.6271
La1–O	2.6576	2.6792	2.6740	2.6504
La2–O	2.6306	2.6765	2.6135	2.6481
La3–O	2.4987	2.5012	2.4931	2.4965

oxygen vacancy and interstitial migration between adjacent sites. In this way, the saddle-point configuration may be identified, from which the energy barrier to migration is derived. The merit of our simulation approach is that it models local lattice relaxation around the migrating oxygen ion and, therefore, the structure is not treated simply as a hard-sphere lattice of fixed ions. The calculated activation energies for oxygen ion migration have been correlated with the available experimental values and are reported in Table 2.

Two main points emerge from these results. First, the correlation between simulation and experiment strongly suggests that the lower conductivity and higher activation energy ($>$ 1.1 eV) in $La_8Sr_2Si_6O_{26}$ is *via* a vacancy mechanism with a negligible population of oxygen interstitial ions in this phase. The lowest energy route for vacancy migration is predicted to be a linear path, with saddle-points mid-way between the O5 positions.

Second, O^{2-} interstitial migration through the channels is predicted for $La_{9.33}Si_6O_{26}$ with significantly lower activation energy. The bulk activation energy in polycrystalline $La_{9.33}Si_6O_{26}$ has been reported as 0.65 eV [5] and 0.74 eV [2]. It is worth noting that Nakayama *et al.*[15] have studied single crystals of the neodymium analogue, $Nd_{9.33}Si_6O_{26}$, and find conductivity parallel to the *c*-axis has an activation energy of 0.62 eV. This accords well with our calculated value of 0.56 eV for oxygen interstitial migration through the *c*-axis channel of $La_{9.33}Si_6O_{26}$.

The lowest energy migration path for the O^{2-} interstitial is predicted to be a non-linear ("sinusoidal-like") mechanism (Fig. 2). This pathway involves migration across the face of a silicate tetrahedral unit, coupled with considerable local relaxation. From our analysis of the saddle-point configuration we find displacements of 0.2 and 0.6–1.0 Å for the Si and the nearest oxygen ions (O1, O3, O4) respectively; these displacements are generally away from the channel and towards the cation-deficient La1/La2 positions, which may indicate the influence of the La vacancies in $La_{9.33}Si_6O_{26}$ as proposed previously.[2,3]

Table 2 Calculated and experimental activation energies for oxygen ion migration

	Activation energy/eV	
Composition	Calculated	Experimental[2,5]
$La_8Sr_2Si_6O_{26}$	1.26[a]	1.14
$La_{9.33}Si_6O_{26}$	0.56[b]	0.65; 0.74

[a] Vacancy mechanism. [b] Interstitial mechanism.

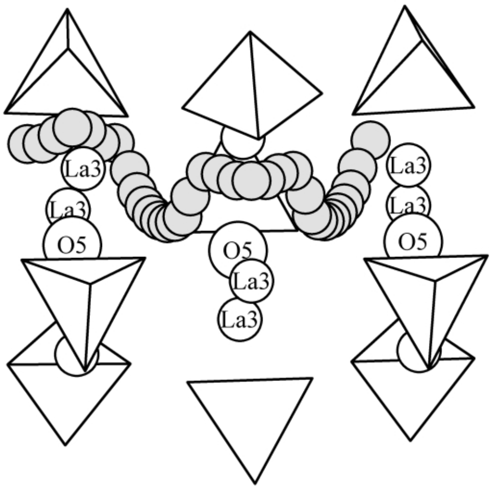

Fig. 2 Oxygen interstitial migration viewed perpendicular to the O5 channel showing a non-linear (sinusoidal-like) pathway.

This suggests that local co-operative relaxation of the $[SiO_4]$ tetrahedra is an important factor for facile oxygen ion conduction, which would be difficult to extract from experiment alone.

In summary, our simulation study has allowed us to gain significant insight as to the oxide ion migration mechanisms in the silicate-based apatites, which are part of a new family of oxygen ion conductors. The calculated energetics suggest that the high ionic conductivity in the apatites of non-stoichiometric composition, such as $La_{9.33}Si_6O_{26}$, is mediated by oxygen interstitial migration (along a non-linear pathway). Our simulations thereby provide a rationalisation based on quantitative calculations, as opposed to qualitative arguments, as to the transport mechanism at the atomic level. This study forms part of the continuing effort to improve our understanding of structure–property relationships in ionic-conducting oxides for potential fuel cell applications.

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