

# Preliminary Results of Molecular Dynamics Simulations of Yttria Doped Ceria

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## Abstract

Preliminary results of molecular dynamics (MD) simulations of the super-ionic system  $(CeO_2)_{1-x}(YO_{1.5})_x$  are reported. Analysis of diffusion in the  $O^{2-}$  sub-lattice, as determined from study of the mean square displacement as a function of the time, suggest that the magnitude of diffusion is strongly dependent on the dopant configuration.

## Introduction

Studies of fluorite oxides doped with yttria and rare earth oxides show the conductivity to depend markedly on the concentration of dopant [1,2]. The most characteristic feature is the conductivity maximum, which, in the case of yttria doped ceria, occurs at approximately 5-8% dopant. This maximum has been found to be closely related to the activation enthalpy which goes through a minimum at approximately the same concentration [1,2].

Studies by Murray [3] and Murray, Murch and Catlow [4] using the combined HADES/Monte-Carlo technique have been quite successful in reproducing this conductivity maximum. Among the more interesting results was the observation that a fully ordered  $Y^{3+}$  distribution (at 14.28 mole %) yielded a conductivity 1.5 orders of magnitude lower than that

Table 1: Comparison of calculated and experimental properties  $H_\sigma$  is the effective Arrhenius enthalpy,  $H_m$  is the activation enthalpy to free  $O^{2-}$  migration.  $H_A$  is the effective association enthalpy.

	Shell Model [3]	Rigid-Ion Model	Experiment
$H_m$	0.49 eV	0.55 eV	(0.49 [7] - 0.61 [1] eV)
$H_A$	0.53 eV	0.46 eV	—
$H_\sigma$	1.02 eV	1.01 eV	1.04 eV
Static dielectric constant	20.6	8.4	—

for a random distribution [3]. However, this approach takes no explicit account of kinetic effects which one would expect to be important in a superionic conductor. Accordingly, MD calculations were performed in order to take a direct look at diffusion in doped  $CeO_2$ .

## Short-range potentials

In their simulations Murray et al. [3,4] used Buckingham potentials, coupled with the shell model for ionic polarizability. Their potentials were based on electron-gas calculations. However, the restriction of MD to the rigid-ion approximation results in migration energies which are too high. The following adjustments were therefore made:

1. The  $Ce^{4+} - O^{2-}$  short-range (rigid-ion) potential was adjusted to give correct migration energies, as calculated using the HADES code [5]. It was not possible to simultaneously fit both the static dielectric constant and the barrier to migration.
2. The potential was also fitted to the 0 K lattice constant of 0.5397 nm. The latter was determined by extrapolation of thermal expansivity data [6].
3. The rigid-ion model also results in too large a binding energy for a dopant-vacancy nn cluster. Accordingly, the hardness parameter in the  $Y^{3+} - O^{2-}$  potential was adjusted from its electron-gas value to yield a nn binding energy of 0.46 eV (Table 1).

In other respects the short-range potentials used are the same as those used by Murray et al. [3,4]. Experimental and calculated properties are compared in Table 1. It can be seen that the rigid-ion potentials appear to predict reliable values for those features which one expects to dominate the diffusion of oxygen vacancies.

## Simulation Conditions

The simulation conditions are detailed below:

1. The simulation box consisted of a 4x4x4 cubic arrangement of  $Ce_4O_8$  cells yielding a total of 768 atoms in the undoped lattice.
2. The initial configuration assumed the perfect fluorite structure. The HADES / Monte-Carlo technique found that an ordered distribution of yttrium resulted in a lowering of the conductivity by 1.5 orders of magnitude [3]. Accordingly,  $Y^{3+}$  and  $O^{2-}$  vacancies were positioned randomly.
3. A target temperature of 833 K was employed in order to facilitate direct comparison with the work of Murray, Murch and Catlow [3,4].
4. A lattice constant of 0.5443 nm at 833 K was calculated from thermal expansivity data [6]. The lattice constant was assumed to be independent of dopant concentration.
5. Constant volume conditions were used.
6. A time step of  $\Delta t = 2 \times 10^{-15}$  seconds was employed.
7. The simulation ran for a total of 3000 time steps (6 ps) of which 800 were for thermal equilibration. This would normally be considered quite short for an MD simulation. However, it is statistically equivalent to a 48 ps run with a 2x2x2 cubic box containing 8  $Ce_4O_8$  cells. Moreover, in this preliminary investigation of  $CeO_2$ , we are interested only in the qualitative/semi-quantitative behaviour of diffusion in the  $O^{2-}$  sublattice. Diffusion, as determined from the time dependence of the mean square displacement (MSD), is normally determined adequately in about 2 ps. Analysis of the diffusion over the final 2000 time steps (4 ps) should, therefore, be sufficient for the purposes of this study.

## Results

Simulation runs were performed at a variety of dopant concentrations two or more times. Each run at a given concentration corresponds to a different random distribution of dopants and vacancies. The calculated oxygen diffusion is detailed in Table 2. In the HADES/Monte-Carlo calculations [3,4] a simulation box of 8x8x8 (512)  $Ce_4O_8$  cells was employed. The MD simulations were restricted to a 4x4x4 box for reasons of expense. In the light of evidence that an ordered distribution of dopants can dramatically lower the conductivity [3] we were a little concerned about the effect of the periodic boundary conditions. Averaging over time origins was not performed as this might serve to hide such effects. Instead, diffusion was calculated by a least squares fitting of MSD time dependence.

Table 2: Oxygen diffusion as a function of the dopant concentration

%dopant	Diffusion $10^5 \text{ cm}^2 \text{ sec}^{-1}$			
	run 1	run 2	run 3	run 4
0.78	0.0190*	0.0163	0.0032	0.0000
2.34	0.1419	0.1492*	---	---
3.91	0.4215*	0.2257	---	---
6.25	0.2479	0.2526*	---	---
7.81	0.3743*	0.0202	---	---
10.16	0.4692	0.0627	0.1406	0.8718*
15.63	0.3131	0.7351*	0.6777	---
23.44	1.4122*	0.2126	0.4052	0.1288
31.25	0.2164	1.2429	1.5639*	0.2169

The magnitude of the diffusion is what one would expect for a superionic conductor of this sort. The calculated diffusion is surprisingly sensitive to the initial distribution of vacancies and dopants. Moreover, there appears to be an upper limit to diffusion at any given concentration. This limit is approximately linear in the mole % dopant (\* in Table 2).

Diffusion continues to rise with increasing dopant concentration. Clearly, therefore, the simulation is failing to model some feature of the system which would increase the migration enthalpy. One such feature is the contraction of lattice with increasing mole % dopant. Unfortunately, data for the high-temperature lattice constant dependence on mole % dopant was not available to us. Consequently, we assumed the same % contraction as at 298 K for 20% dopant [8]. Deviations from Vegard's rule were ignored and the lattice constant was determined from the 0% and 20% dopant values by interpolation or extrapolation as appropriate.

Calculations were repeated using the modified lattice constants. This resulted in some improvement, namely a maximum in the conductivity; however, it is too shallow and occurs at too high a concentration of dopant. The diffusion data remain strongly sensitive to the configuration of dopants and vacancies.

Moreover, in both sets of simulations it was found that the  $O^{2-}$  diffusion for a given dopant configuration sometimes varied significantly with time. That is, it was observed that diffusion, proceeding with a particular value of  $D$ , might suddenly adopt a different  $D$  value, or indeed stop altogether ( $D = 0$ ). This phenomenon might be related to trapping of vacancies. The observation that vacancy migration occasionally stops altogether may indicate correlated vacancy motion.

## Discussion

The results of these preliminary simulations are in poorer agreement with experiment that might have been expected. Clearly, the diffusion process is more complicated than at first envisaged. A number of possible explanations may be advanced:

1. The short-range potentials were fitted to the energy barrier to vacancy migration and to the nn dopant-vacancy binding energy. There may be more complicated structures of clusters which are not correctly modelled by this potential.
2. In this type of MD we are limited to approximately 1000 atoms. In this simulation we had 768 atoms in the undoped system - 256  $Ce^{4+}$  and 512  $O^{2-}$ 's. The conductivity maximum occurs at roughly 6% dopant. For 6.25 mole % dopant we have only 16  $Y^{3+}$  dopant ions and 8  $O^{2-}$  vacancies. This is hardly a representative selection of  $Y^{3+}$  and  $O^{2-}$  vacancy environments. This analysis suggests that either bigger simulation boxes are employed or that averages of many simulations for every concentration are taken.
3. A third possibility is that of artificial ordering due to the periodic boundary condition. Murray [3] found using the HADES/Monte-Carlo model that diffusion differs dramatically between ordered and random distributions of dopants. The  $Y^{3+}$  were distributed randomly within the simulation box. However the periodic boundary condition might result in a migrating  $O^{2-}$  vacancy experiencing a pseudo-ordered environment. This consideration also points towards the use of a larger simulation box.

We are currently pursuing these calculations with a view to determining the approximation(s) responsible for the unusual diffusion data.

## Conclusions

1. Yttria doped ceria yields diffusion with sensible values.
2. Results are sensitive to dopant configuration.
3. Poor statistics for dopant ions and vacancies suggest (i) the use of much larger simulation boxes or (ii) averaged results of numerous independent simulations for each concentration
4. The periodic boundary condition may result in artificial ordering, indicating again the use of a larger simulation box.

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