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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking Imperial College, London as follows: The contractor will investigate use of cellular automata (CA) algorithms to predict the growth of surface structures and the effects of the underlying substrate on the surface morphology. Structure/property maps will be generated using atomistic simulation calculations. Three systems will be investigated. First the activation energy for oxygen ion conduction in pyrochlore oxides. Second the stability of the perovskite structure with particular reference to stoichiometry. Third the structure type exhibited by AB2O4 compounds. The results of the research will be presented at the 102nd American Ceramic Society meeting, at a Materials Directorate organized meeting and will be a published in the open literature.

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OXYGEN ION CONDUCTION IN PYROCHLORES

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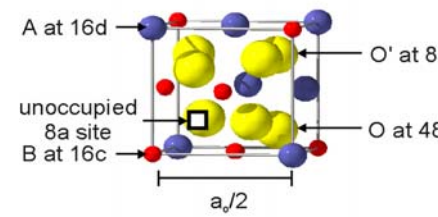
Introduction

$A_2B_2O_7$ pyrochlore materials are being considered for use in applications ranging from oxygen sensors to potential phases for the immobilisation of actinides in nuclear waste and the burning of excess plutonium in reactors. The way in which ions are transported through the lattice is central to each of these applications. Consequently, we are investigating oxygen ion conduction mechanisms using atomic scale computer simulation techniques based on classical pair-potential models. Our aim is to provide data that will optimise the selection of the A and B component cations. For an oxygen ion conductor, this means determining the combination of A and B cations which provides the lowest migration activation energy.

Crystal Structure

- The pyrochlore structure is closely related to fluorite
- Can be considered as an ordered defective fluorite with space group Fd3m.
- Centrosymmetric description of the crystal structure assumes 3+ cations occupying the 16d sites and 4+ cations occupying 16c sites.
- Six oxygen atoms occupy 48f sites, the seventh occupies the 8b position, leaving an unoccupied 8a site.
- There are eight formula units in a full unit cell.



Here, a summary of work predicting activation energies for the migration of an oxygen ion between 48f sites in anion deficient $Gd_2Zr_2O_7$ & related pyrochlores is presented.

Techniques

1. Methodology

The presence of defects causes perturbations of surrounding lattice ions. Calculations of defect energies must therefore account for these structural relaxations. This is achieved by partitioning the lattice into two regions :

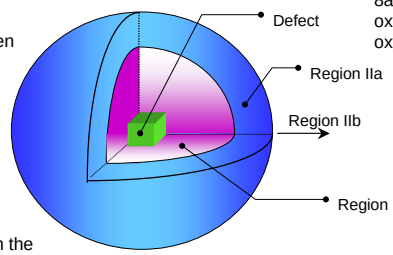
Region I: ions treated explicitly and relaxed to zero strain.

Region IIa: forces between ions determined via the Mott-Littleton approximation, ions are relaxed to zero strain.

Region IIb: provides the Madelung field of the remaining crystal, relaxation energy determined using Mott-Littleton.

In Region I, the interaction between two ions, i and j is given by:

$$U_L = \frac{1}{4\pi\varepsilon_o}\sum_{i\neq j}\frac{q_i q_j}{r_{ij}} + Ae^{-r_{ij}/\rho} - \frac{C}{r_{ij}^6}$$

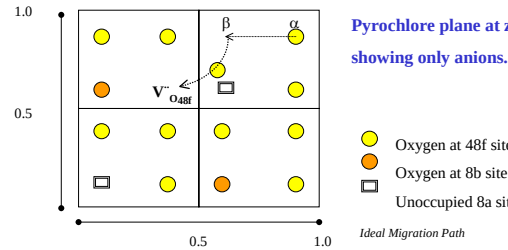


Where A, ρ and C are adjustable parameters, r_{ij} is the interionic separation and q is the charge on the ion. The adjustable parameters were chosen to accurately reproduce the lattice parameters of 53 pyrochlore structures.

2. Migration Mechanism

Oxygen ion conduction in pyrochlores proceeds via an oxygen vacancy mechanism. The vacancies may be formed via intrinsic Frenkel disorder, reduction or nonstoichiometry. The migration mechanism consists of successive jumps of oxygen ions into vacant sites. These oxygen ions may move from 48f to a vacant 48f site, from 48f to a vacant 8b site or from 8b to a vacant 48f site. This motion may be assisted by intermediate occupation of the unoccupied 8a site.

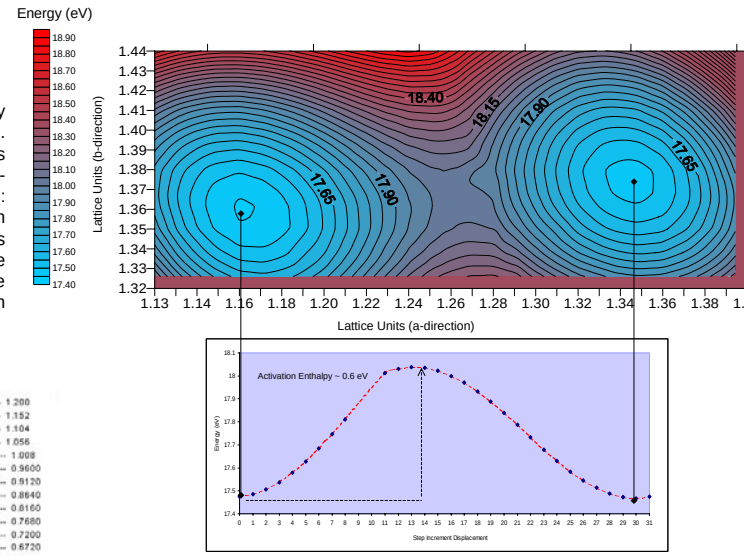
Here we have modelled the 48f - 48f mechanism, the only one which alone may form a continuous migration path through the crystal. The figure below shows schematically how a vacant 48f site becomes associated with the displacement of a 48f oxygen towards an 8a site (the extent of displacement varies for each material). Thus, migration of the α - 48f oxygen to the β - 48f oxygen site forces the displaced 48f oxygen ion into the vacant 48f oxygen site.

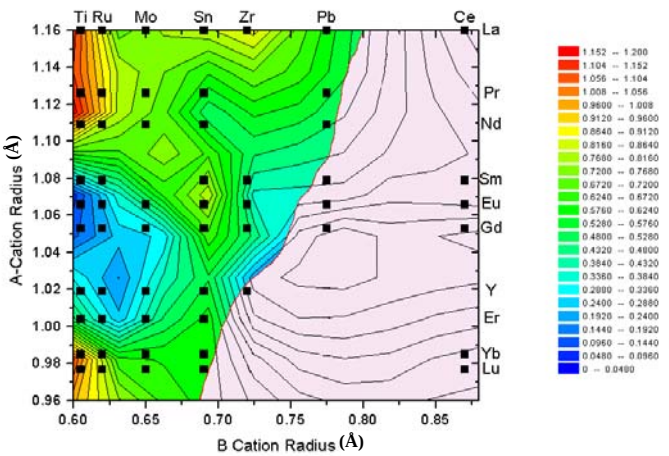


Results & Discussions

Migration Energies for 48f - 48f jumps

The energy contour map opposite shows the minimum energy route taken by an oxygen ion migrating between α and β 48f sites in $Gd_2Zr_2O_7$ pyrochlore. The graph below the contour map shows the activation energy which is approximately 0.6eV, comparable to experimental values quoted ~ 0.73 - 0.83 eV. The same calculation was repeated for 56 $A_2B_2O_7$ compounds: A=Lu to La , B= Ti to Ce. These results are presented below in the form of an energy contour map. The y-axis shows A - cation radius, the x-axis shows B - cation radius. Equal activation energies are connected by contours. The black points are compounds for which a calculation was made. Points to the left of the red line represent experimentally stable pyrochlore forming cation combinations, points to the right form disordered fluorite structures.





The results suggest that compounds with low B - cation radii but with A - cation radii of intermediate size exhibit the lowest migration activation energies for this pathway. In contrast, compounds with low B - cation radii and with either very large or very small A - cation radii, exhibit high activation energies for migration (of the order of 1eV or more).

Compounds of intermediate B - cation radii (e.g. Sn) show less variation in activation energy as a function of A - cation radius. There is the suggestion that compounds with higher B - cation radii might present lower activation energies. However, the effect of disorder on activation energy may become significant - more work is required before definite conclusions can be made.