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Title: The Stability of Pyrochlore Oxides

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THE STABILITY OF PYROCHLORE OXIDES

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A Contour plot of the disorder reaction energies across a wide variety of $A_2B_2O_7$ pyrochlore oxides has been produced using atomistic simulation calculations based on energy minimization techniques. Cations studied range from Lu^{3+} to La^{3+} on the A site and Ti^{4+} to Ce^{4+} on the B site. The results relate the experimentally observed stability range of the pyrochlore structure to A and B cation size and disorder. Disorder enthalpies decrease dramatically with increasing B cation size whilst the rate of increase with A cation size depends markedly on the particular B cation. The association of anion Frenkel and cation antisite disorders is found to be of importance.

1. INTRODUCTION

A large number of ternary oxides with the formula $A_2B_2O_7$, where A is a 3+ ion and B is a 4+ ion, adopt the pyrochlore structure. Elemental versatility ensures that pyrochlore compounds exhibit a variety of interesting properties. A few of the applications for which pyrochlores have been candidates are: fluorescence centers¹, catalysts^{2,3}, actinide host phase in nuclear waste^{4,5} and as both cathode and electrolyte materials in solid oxide fuel cells⁶⁻⁸.

Previously there has been a trend in delimiting the pyrochlore stability field by a simple consideration of the cation radius ratio $r(A^{3+})/r(B^{4+})$. The radius ratio is generally chosen empirically to best fit the available experimental data^{9,10}. However, this does not take into account the effects of oxygen sublattice relaxation, which may be significant. We wish to propose alternative methods of determining pyrochlore stability based on energy minimization calculations.

1.1 Crystallography

The general formula of oxide pyrochlores is written as $A_2B_2O_6O'$. The space group is Fd3m with the unit cell containing 8 molecules ($Z=8$) and four crystallographically non-equivalent sites. When the origin is fixed on the B site the atoms occupy the following special positions: A at 16d, B at 16c, O at 48f and O' at 8b. 48f oxygen ions are characterized by a positional parameter x .

The most popular depictions of the pyrochlore structure are those based on a fluorite type cell. In this description the structure is equivalent to an ordered defective fluorite. The A and B cations form the face-centered cubic array and are ordered into rows in $\langle 110 \rangle$ directions. (In defective fluorites the seven oxygen atoms are tetrahedrally coordinated by four random cations and evenly distributed over eight equivalent oxygen sites.) In the pyrochlore structure two different oxygen sites occur. Six oxygen atoms occupy the 48f sites surrounded by two A cations and two B cations while the seventh oxygen atom occupies the 8b site and is surrounded by four A cations. The remaining unoccupied 8a site is surrounded by B cations. Finally, the 48f anions are shifted towards the smaller B cations by an amount defined by the $x(48f)$ positional parameter. In the ideal fluorite structure, the position parameter $x = 0.375$. Figure 1 shows one eighth of a unit cell of the pyrochlore structure; this partial unit cell is analogous to a single fluorite unit cell.

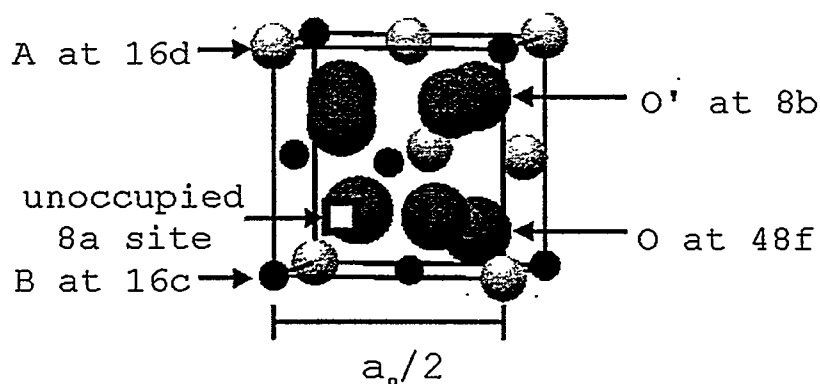


Figure 1 Partial unit cell of pyrochlore structure

2. METHODOLOGY

Atomistic computer simulation techniques, based on energy minimization with a Born like description of the lattice¹¹, are used to generate the various structures. The procedures are based upon a description of lattice forces in terms of effective potentials. The perfect lattice is generated by defining a unit cell that is repeated throughout space using periodic boundary conditions as defined by the usual crystallographic lattice vectors. The total energy of the crystal is minimized by allowing the ions in the unit cell and the lattice vectors to relax to zero strain.

We consider interactions due to long range Coulombic forces, which are summed using Ewald's method¹² and short range forces, that are modeled using parameterized pair potentials, S_{ij} . In order to reduce the computational time the short range interactions are set to zero beyond 20 Å. In this study the

Buckingham potential form was used,

$$S_{ij} = A \exp(-r_{ij}/\rho) - C/r_{ij}^6 \quad (1)$$

where A, ρ and C are three adjustable parameters (see Table 1).

Table 1 Short-range potential parameters

| Species | A (eV) | ρ (Å) | C (eVÅ ⁶) |
|-----------------------------------|---------|------------|-----------------------|
| O ²⁻ -O ²⁻ | 9547.96 | 0.2192 | 32.0 |
| Lu ³⁺ -O ²⁻ | 1618.80 | 0.33849 | 19.27 |
| Yb ³⁺ -O ²⁻ | 1649.80 | 0.3386 | 16.57 |
| Er ³⁺ -O ²⁻ | 1739.91 | 0.3389 | 17.55 |
| Y ³⁺ -O ²⁻ | 1766.40 | 0.33849 | 19.43 |
| Gd ³⁺ -O ²⁻ | 1885.75 | 0.3399 | 20.34 |
| Eu ³⁺ -O ²⁻ | 1925.71 | 0.3403 | 20.59 |
| Sm ³⁺ -O ²⁻ | 1944.44 | 0.3414 | 21.49 |
| Nd ³⁺ -O ²⁻ | 1995.20 | 0.3430 | 22.59 |
| La ³⁺ -O ²⁻ | 2086.01 | 0.3430 | 23.94 |
| La ³⁺ -O ²⁻ | 2088.79 | 0.3460 | 23.25 |
| Ti ⁴⁺ -O ²⁻ | 2131.04 | 0.3038 | 0.0 |
| Ru ⁴⁺ -O ²⁻ | 1215.78 | 0.3441 | 0.0 |
| Mo ⁴⁺ -O ²⁻ | 1223.97 | 0.3470 | 0.0 |
| Sn ⁴⁺ -O ²⁻ | 1414.32 | 0.3479 | 13.66 |
| Zr ⁴⁺ -O ²⁻ | 1502.11 | 0.3477 | 5.1 |
| Pb ⁴⁺ -O ²⁻ | 1640.34 | 0.3507 | 19.50 |
| Ce ⁴⁺ -O ²⁻ | 1809.68 | 0.3547 | 20.40 |

In addition to studying the perfect lattice, this approach can be used to predict how the lattice accommodates defects. To do this lattice is partitioned into two regions: a spherical inner region, I, at the center of which the defect is introduced, and an outer region, II, which extends to infinity. In Region I, interactions are calculated explicitly so that the response of the lattice to the defect is modeled by relaxing the positions of all ions to zero force using a Newton-Raphson minimization procedure. The response of Region II is treated using the Mott-Littleton approximation¹³.

The polarizability of the ions may be accounted for via the shell model¹⁴. This consists of a massless shell with charge $X|e|$ that is allowed to move with respect to a massive core of charge $Y|e|$; the overall charge state of each ion is therefore equal to $(X+Y)|e|$. The core and shell charges are connected by an isotropic harmonic spring force of constant k . Displacement of the shell relative to the core gives a good description of electronic polarization. In

all calculations, O^{2-} and the larger 4+ cations (Zr, Pb, Ce) are treated as polarizable using the shell model: for O^{2-} , $Y = -2.04$, $k = 6.3 \text{ eV \AA}^{-2}$; Zr^{4+} , $Y = -0.05$, $k = 189.7 \text{ eV \AA}^{-2}$; Pb^{4+} , $Y = -0.05$, $k = 205.0 \text{ eV \AA}^{-2}$; Ce^{4+} , $Y = -0.20$, $k = 177.84 \text{ eV \AA}^{-2}$.

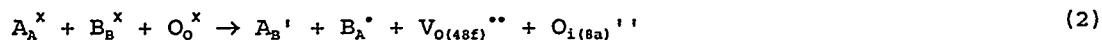
For further details of the computational methods see references 15 and 16. In all cases, calculations were carried out using the CASCADE code¹⁷.

3. RESULTS AND DISCUSSION

Our initial aim was to generate a contour plot of the disorder defect energy as a function of A and B cation radii. Through this we should obtain insight into the stability range of the pyrochlore structure with respect to defect energies. In previous studies^{9,10} a cation radius ratio argument, $r(A^{3+})/r(B^{4+})$, is invoked to explain this stability range; however, $r(A^{3+})/r(B^{4+})$ plotted against $r(A^{3+})$ and $r(B^{4+})$ is necessarily a straight line which cannot account for subtle relaxation effects. In addition there is not a good analytical rationale for choosing the best $r(A^{3+})/r(B^{4+})$ ratio.

When considering pyrochlore compounds the data set is extensive but not uniform. The present study ranges in ion size from lanthanum to lutetium on the A site and titanium to cerium on the B site. Ion sizes (radii) are those given by Shannon¹⁸ and are taken to be VIII-coordinate for the B cation and VI-coordinate for the A cation. Gaps arise in this data set because: (1) some $A_2B_2O_7$ compounds do not form cubic pyrochlores and (2) Zr, Pb, and Ce do not form pyrochlores with the larger 3+ cations. Unfortunately, it was found that a reliable contour plot could not be achieved if these hypothetical compounds are excluded. Essentially the number and distribution of data points is such that extrapolation cannot proceed far enough beyond the data set for the contour plot to be useful. The nature of the present calculations has enabled us to generate the missing data points by using potentials derived from experimentally observed pyrochlore compounds to investigate hypothetical pyrochlore compounds.

Cation disorder increases the similarity between non-equivalent oxygen sites. Thus it has been proposed by Wilde and Catlow¹⁹ that the presence of cation disorder will decrease the anion Frenkel energy.



Our calculations support this view, with the presence of a cation antisite pair adjacent to an anion Frenkel pair greatly reducing the anion Frenkel energy.

Figure 2 shows the contour map for the formation energy of a clustered cation antisite pair adjacent to an anion Frenkel pair as a function of A and B

cation radii. The thick light contour on the right side of Figure 2 defines a boundary for the calculated stability of the ternary compound with respect to the binary oxides,



A negative reaction enthalpy indicates stability so that stable compounds lie to the left of the contour while unstable compounds lie to the right of this contour. This immediately eliminates the possibility of forming the cerate pyrochlores, except for $La_2Ce_2O_7$, and $A_2Pb_2O_7$ where $A = Lu, Yb, Er$.

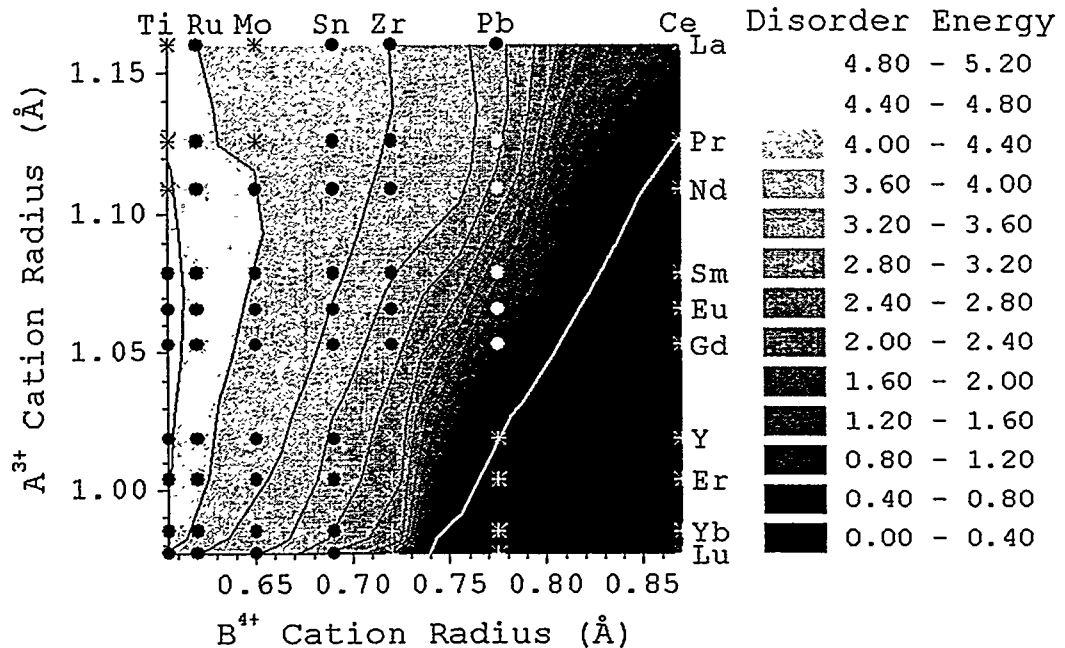


Figure 2 Contour map of the defect formation energy for an anion Frenkel pair adjacent to a cation antisite pair

Pyrochlore compounds observed experimentally are shown as black circles. Pyrochlore compounds for which experimental data is not available but for which calculations have been carried out are shown as white crosses. White circles indicate compounds that have been synthesized by high pressure techniques (300 MPa, 700°C)²⁰. Non-cubic $A_2B_2O_7$ compounds are shown as black crosses: in these cases, calculations predict the cubic phase to be stable with respect to the binary oxides, but experimentally a non-cubic phase is observed. Non-cubic phases have not been thoroughly characterized crystallographically and hence calculations have not been attempted on these phases. Thus it appears that equation 3 predicts the stability of a number of materials incorrectly. However, equation 3 does not consider that such materials may be stable solutions as disordered fluorites or may undergo non-cubic distortions that are more stable than the simple cubic structure.

The most striking feature that arises from Figure 2 is that for some compounds the defect energy is actually negative. Furthermore, there is now a clear plateau of stability so that beyond a critical combination of A and B cation radii a further increase in B radius or decrease in A radius quickly destabilizes the pyrochlore structure. Thus certain combinations of A and B cations which are to the left of the black line (the reaction enthalpy is negative) will nevertheless form disordered fluorites; i.e. there is no driving force for cation ordering in these compounds because the introduction of defects via disorder processes is energetically favorable. Of course, a disordered fluorite region will also include materials where the disorder reaction enthalpy is small, yet positive, since the driving force for ordering may not be great enough to overcome kinetic barriers. Although an appropriate cutoff in disorder enthalpy has not yet been determined theoretically, comparison with experimental data in Figure 2 suggests a contour value of ~ 2.6 eV (~ 0.7 eV per defect). Given the approximate nature of our theoretical technique we do not intend for this energy value to be regarded as absolute but rather as relative.

Figure 2 also shows that the lead compounds synthesized by high pressure techniques exhibit lower disorder energies than existing compounds synthesized at atmospheric pressure. These high pressure compounds clearly have comparable energies to the hypothetical Zr pyrochlores which makes further high pressure syntheses an intriguing prospect.

4. CONCLUSIONS

It is now possible, based on disorder formation energies, to subdivide the stability range of compounds as a function of A and B cation radii into four regions. Compounds in the region where the reaction enthalpy is positive will never form ordered pyrochlore oxides of the form $A_2B_2O_7$. They may, of course, still form extensive $A_2O_3:BO_3$ solid solutions. Compounds whose disorder enthalpies lie above an energy contour (relative to the full ionic model) of ~ 2.6 eV (~ 0.7 eV per defect) will form ordered pyrochlore structures at atmospheric pressure. There is then an intermediate transition region where compounds will remain defective fluorites. Finally, compounds with large $r(A^{3+})/r(B^{4+})$ values, i.e. composed of large A cations and small B cations, seem to form non-cubic unit cells. The exact boundary of this fourth region is not yet clear.

The disordered transition region provides us with some exciting experimental challenges. It includes compounds that have been synthesized by high pressure

techniques, compounds in which micro-ordering has been observed and compounds in which pyrochlore ordering has never been observed. Thus, if the present analysis is correct in that these compounds remain disordered due to an insufficient driving force for ordering, given appropriate conditions, such as high pressure, it should be possible to overcome kinetic barriers and form ordered or partly ordered pyrochlore structures.

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