Chapter 4

Relative Stabilities of Pyrochlore $(A_2B_2O_7)$, Disordered Fluorite $([AB]_2O_7)$ and the δ -Phase $(A_4B_3O_{12})$

4.1 Introduction

Materials with the fluorite BO_2 and disordered fluorite structure $(AB)_2O_{8-x}$ have been found to be remarkably resistant to radiation induced amorphisation [126–129]. Using this nomenclature A represents a trivalent cation and B represents a tetravalent cation. Examples of these include UO_2 [126], monoclinic zirconia [127], cubic stabilized zirconia [127–129], $Y_2Ce_2O_7$ and $La_2Ce_2O_7$ [130], and $Er_2Zr_2O_7$ [131,132]. Although at first glance these last three material my appear to be pyrochlore (discussed next), they actually form in the disordered fluorite structure [130]. Due to this high radiation tolerance, they have been considered for combined inert matrix fuel forms and wasteforms for the "burning" and final disposal of Pu and the minor actinides [133,134].

Pyrochlore (A₂B₂O₇) compounds are related to the fluorite structure and the nature of this relationship will be considered in the crystallography section (section 4.2.1). They form over a huge compositional range due to the flexibility of the structure and this was explored in depth in the review by Subramanian [135]. As stated earlier, the pyrochlores considered in this study are formed by combining a trivalent "A" cation and a tetravalent "B" cation although pyrochlores can also form in the $A^{2+}{}_{2}B^{5+}{}_{2}O_{7}$ stoichiometry [135]. Due to this wide compositional range, pyrochlore compounds have many different properties and they have been used, or are being put forward as materials for use in diverse applications including solid electrolytes [136–140], anodes [140–144] and cathodes [140, 145–147] for fuel cells and sensors, catalysts [148–150], dielectrics [151–155] and materials for the encapsulation of actinides and other nuclear wastes (see chapter 5).

Another fluorite related phase which also forms in the A_2O_3 -BO₂ system is the δ -phase. Unlike the pyrochlore system which has been studied extensively, much less is known about these compounds. There have only been a few studies into this system, mainly as passing interest in technologically important systems like indium-doped tin oxide (ITO) [156] and cubic stabilised

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zirconia [157–159]. There have been a few studies specifically aimed at compounds in this system including the study by Lopato *et al.* [160] in which the synthesis and thermal expansion properties of these phases were determined and a study by Thornber *et al.* [161] in which the crystal structures of $Sc_2Zr_5O_{13}$ and $Sc_4Zr_3O_{12}$ were determined.

In order to understand these related materials better, it is important to know what phases will be formed when a mixture of simple oxides are combined (synthesis). For example, when Yb₂O₃ and ZrO₂ are combined, will a δ -phase or a pyrochlore or a fluorite structure result? In this chapter, an extensive range of compositions will be investigated using atomistic simulation in order to provide greater insights into this complicated question. The results will be plotted in the form of a phase map in which A cations, ordered by ionic radius are shown, increasing along the *y*-axis, B cations, also ordered by ionic radius, increase along the *x*-axis and the points on the map indicate compounds simulated. The colour of the point will indicated which phase is most stable. This information can then be used to guide experimental studies into the relative radiation durabilities of the corresponding materials which can then be use to gauge potential performance+ as a wasteform material

4.2 Literature Review

4.2.1 Crystallography

The fluorite, pyrochlore and δ phases are all related. As the stoichiometry changes from BO₂ to A₂B₂O₇ to A₄B₃O₁₂ the anion to cation ratio decreases and is shown in table 4.1. It is easy to see how this has been achieved going from the fluorite to the pyrochlore phases as they are conceptually similar but the δ -phase is more difficult to visualise. Figure 4.1 shows a full unit cell of the fluorite structure and figure 4.2 shows an idealised 1/8 unit cell of pyrochlore with all the oxygen ions at the positions they would occupy if it had adopted the fluorite structure. From these it is clear that one of the oxygen ion positions that was occupied in the fluorite structure is now absent and the cation sublattice now exhibits an alternating ABAB pattern. This results in a doubling of the cubic unit lattice parameter from approximately 5 to 10Å.

Table 4.1: Anion to cation ratios from fluorite to δ -phases. M represents any metal, or the number of cations.

Compound	Stoichiometry	Anion - Cation Ratio
Fluorite	MO_2	2.000
Pyrochlore	M_4O_7	1.750
δ -phase	M_7O_{12}	1.714

The structure in figure 4.2 is an idealised version to aid comparison and does not show the way way in which the anions restructure around the 8a site or how the structure orders. This is shown in figure 4.3. The figure was generated used the structural data for $Gd_2Sn_2O_7$ from Kennedy *et al.* [162]. Part a) of this figure shows that the 48f oxygen ions relax away from their ideal fluorite position, moving towards the unoccupied site (the 8a site in fluorite). The degree of relaxation is termed the x parameter as it refers to the condition of the 48f site coordinates $(x, \frac{1}{8}, \frac{1}{8})$ [163]. The ideal fluorite positions occur with an x parameter of 0.375 and this idealised structure is shown in Figure 4.3b) which also makes the cation ordering of the system clear. For Gd₂Sn₂O₇ the value of x is 0.3348 [162].



Figure 4.1: The Fluorite Structure. Small yellow spheres are B^{4+} ions, large red spheres are O^{2-} ions.



Figure 4.2: The Pyrochlore Structure (1/8 unit cell). Larger blue spheres are A^{3+} ions, small yellow spheres are B^{4+} ions, large red spheres are O^{2-} ions.



Figure 4.3: The Pyrochlore Structure (Full unit cell). a) Showing relaxed $Gd_2Sn_2O_7$ positions (x = 0.3348). b) Showing idealised fluorite positions (x = 0.375).

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As mentioned earlier there are compounds that form with the pyrochlore stoichiometry $(A_2B_2O_7)$ but do not actually form in the cubic pyrochlore structure. There are at least 2 variants, one is the disordered fluorite ($[AB]_2O_7$) which tends to form in the large B cation, small A cation region and the other forms a monoclinic structure which tends to form in the large A cation, small B cation region of the compositional space.

The disordered fluorite structure exhibits the Fm3m space group and has 50% A and B cation occupancy on the cation sublattice and a $\frac{7}{8}$ occupancy on the 8c oxygen sublattice [164, 165]. Figure 4.4 shows a schematic of the disordered fluorite structure generated using structural data from [164].



Figure 4.4: The Disordered Fluorite Structure. Mixed A and B cations randomly distributed over the cation sublattice are determined by yellow/blue hemispheres and the $\frac{7}{8}$ occupied O sublattice is represented by red spheres.

The monoclinic structure forms in the $P2_1$ space group and structural data has been derived by Schmalle *et al.* [166] for the La₂Ti₂O₇ compound. The structure is shown in figure 4.5.



Figure 4.5: The Monoclinic Pyrochlore Structure. Light blue spheres are A^{3+} ions, dark blue spheres are B^{4+} ions, red spheres are O^{2-} ions. a) Perspective view, b) view down the c-axis. Created using structural data from Schmalle et al. [166]

The δ -phase (A₄B₃O₁₂) forms in a rhombohedral structure (in the R $\bar{3}$ space group) although it is more commonly represented in a hexagonal form [1, 156–161,167]. Until recently the structure was usually defined as per Red'ko and Lopato [1] (data for Sc₄Zr₃O₁₂ reproduced in table 4.2). These authors define the cation sublattices a disordered mixture of Sc and Zr. Two theoretical studies by Bogicevic *et al.* [158] and Bogicevic and Wolverton [157] have refined this further for Y₄Zr₃O₁₂ and Sc₄Zr₃O₁₂ respectively to produce coordinates which can be represented in the R3 space group without disordered cations. This makes it possible to run computer simulations that can easily be compared with systems that are not disordered. The data for Sc₄Zr₃O₁₂ is shown in table 4.3 and a graphical representation is shown in Figure 4.6.

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	Ion	Site	x	y	z	Occupancy
	$Zr^{4+}(1)$	3a	0.0000	0.0000	0.0000	0.429
	$Sc^{3+}(1)$	3a	0.0000	0.0000	0.0000	0.571
	$Zr^{4+}(2)$	18f	0.2903	0.4096	0.0161	0.428
	$Sc^{3+}(2)$	18f	0.2903	0.4096	0.0161	0.572
	$O^{2-}(1)$	18f	0.2990	0.4530	-0.2300	1.000
	$O^{2-}(2)$	18f	0.3010	0.4540	0.2780	1.000

Table 4.2: Crystal Structure of Sc₄Zr₃O₁₂. Space Group R $\overline{3}$, a = b = 9.396Å, c = 8.706Å $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$. Reproduced from Red'ko and Lopato [1].

Table 4.3: Crystal Structure of Sc₄Zr₃O₁₂. Space Group R3, a = b = 9.532Å, c = 8.823Å $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$. adapted from Bogicevic and Wolverton [157].

Ion	Site	x	y	z	Occupancy
$Zr^{4+}(1)$	3b	0.6159	0.5445	0.6840	1.0
$Sc^{3+}(1)$	3b	0.8817	0.5877	0.9832	1.0
$Sc^{3+}(2)$	1a	0.6667	0.3333	0.3247	1.0
$O^{2-}(1)$	3b	0.0376	0.8204	0.8886	1.0
$O^{2-}(2)$	3b	0.3086	0.8440	0.7823	1.0
$O^{2-}(3)$	3b	0.6375	0.5208	0.9397	1.0
$O^{2-}(4)$	3b	0.8424	0.5436	0.7252	1.0



Figure 4.6: The Ordered δ -phase Structure. Light blue spheres are A^{3+} ions, dark blue spheres are B^{4+} ions, red spheres are O^{2-} ions. a) perspective view, b) view down c-axis.

4.2.2 Experimental Work

There has been a great deal of experimental work focusing on pyrochlores and fluorites, ranging from full scale phase diagram construction to structural studies using X-ray and neutron diffraction. Comparatively, less work has been performed on the δ -phase and the boundaries between the pyrochlore phase and δ -phases are uncertain. Some of the structural studies and phase diagrams will now be summarised and discrepancies highlighted.

Phase diagrams

There have been quite comprehensive studies on the titanate, hafnate and zirconate systems and some examples of these are show in figures 4.7 to 4.18. These figures will now be examined in order of B cation radius as they will appear in the results.

The titanate systems show a compound with pyrochlore stoichiometry ranging all the way from A cations Nd to Lu, even though, according to Subramanian [135], Nd₂Ti₂O₇ does not form in the cubic system. By examining figures 4.7, 4.8 and 4.9 it is possible to see both common features and differences which will now be discussed. They all predict formation temperatures for the pyrochlore compounds to be about 1800 °C and the existence of the A_2TiO_5 compound.



Figure 4.7: Phase Diagrams of A_2O_3 - TiO₂ systems, A = Lu, Ho, Dy and Nd. All showing a $A_2Ti_2O_7$ pyrochlore phase. Reproduced from [168–170]. C = cubic bixbyite, P = pyrochlore, R = rutile, F = fluorite, NT = Nd₂TiO₅.

All the systems in figure 4.7 show the pyrochlore as a line compound indicating no solid solution with either A_2O_3 or TiO_2 at any temperature, however, the Y_2O_3 - TiO_2 system shown in figure 4.8 shows a limited solid solubility.

It is tempting although incorrect to draw conclusions about differences between related but chemically different systems. Figure 4.9 shows 2 phase di-



Figure 4.8: Phase Diagram of Y_2O_3 - TiO₂ system, reproduced from [171]. Y = Y_2O_3 , P = pyrochlore, T = TiO₂ (rutile).

agrams for the Sm_2O_3 - TiO₂ system generated by different research groups and gives a good opportunity for comparison. There are quite obvious differences between the work by the different groups, one indicating the pyrochlore as a line compound, similar to the systems described in Figure 4.7, and the other showing a region of solid solution.



Figure 4.9: A comparison of $2 \text{ Sm}_2\text{O}_3$ - TiO₂ phase diagrams from different research groups. a) reproduced from [172]. b) reproduced from [173].

A very comprehensive set of phase diagrams is found by moving up in B cation radius to examine the A_2O_3 - HfO₂ systems. While Hf compounds were not specifically modelled in this study, the ionic radius of Hf⁴⁺ is 0.71 Å which places it in between Sn⁴⁺ (0.69 Å) and Zr⁴⁺ (0.72 Å), (ionic radii from Shannon [174]). This means that it is possible to interpolate between the two to generate results for Hf. By looking at the phase diagrams in figures 4.10 to 4.13 it is clear that the region of pyrochlore stability has significantly changed with respect to the titanate systems in that the pyrochlore phase is only stable for smaller A cations ranging from La to Tb.

Figure 4.10 shows phase diagrams in the system A_2O_3 - HfO_2 where the A cation is small. It can be noted here that all of these systems show an extensive fluorite solid solution field and no pyrochlore phase. These phase



Figure 4.10: Phase diagrams of A_2O_3 - HfO₂ systems with small A^{3+} cations, A = Lu, Yb, Er and Ho. Reproduced from [175]. C = cubic bixbyite, F = fluorite, H = hexagonal, M = monoclinic, T = Tetragonal.

diagrams are all in the very high temperature region and none show any temperatures below 1700 °C. Whilst this should be low enough to show the formation of a pyrochlore phase (should one exist for these compositions), it is not enough to allow the formation of the δ -phase which tends to form between 1100 and 1600 °C [160, 167].

More recently Duran and Pascual [167] have revisited the Yb₂O₃ - HfO₂ system, taking measurements at significantly lower temperatures. By doing this they managed to identify both the δ -phase Yb₄Hf₃O₁₂ and another compound with hexagonal symmetry, Yb₆HfO₁₁. Duran and Pascual [167] also

progressively heated the δ -phase to 1600 \pm 25 °C whereupon it underwent an order-disorder transformation to the disordered fluorite structure.



Figure 4.11: Phase diagram of the Yb_2O_3 - HfO_2 system. Reproduced from [167].

Lopato *et al.* [160] have performed a more detailed study considering just the δ -phase compounds and they found that, in the hafnate system, the δ -phase forms for A cations ranging from Sc to Er but specifically not for Ho and Dy. It would therefore be prudent to expect that, if low temperature phase diagrams were plotted for the other systems in figure 4.10, except perhaps

the Ho_2O_3 - HfO_2 system, that they would contain features similar to figure 4.11.

Figure 4.12 shows the hafnate systems for A cations with intermediate radii; Dy, Tb, Gd and Eu. In this figure the transition between pyrochlore-forming and non-pyrochlore forming compositions can be seen. All of these phase diagrams predict an order-disorder transition between the fluorite phase and the pyrochlore phase (where it exists) and that as the A cation become larger, the transition temperature moves higher.



Figure 4.12: Phase diagrams of A_2O_3 - HfO₂ systems with intermediate A^{3+} cations, A = Dy, Tb, Gd and Eu. Reproduced from [176, 177]. C = cubic bixbyite, B = B-rare earth, H = hexagonal, F = fluorite, M = monoclinic, T = tetragonal, P = pyrochlore.

Figure 4.13 is the final figure based on the hafnate system and looks at the larger A cations including, Sm, Nd Pr and La. In this series, the pyrochlore phase becomes stable all the way up to the liquidus temperature and thus no longer exhibits a solid state order-disorder transition. The extent of solid solutions is also quite pronounced unlike in the titanate phases.



Figure 4.13: Phase diagrams of A_2O_3 - HfO₂ systems with large A^{3+} cations, A = Sm, Nd, Pr and La. Reproduced from [178]. A = A-rare earth, B = B-rare earth, P = pyrochlore, H = hexagonal, F_1 and $F_2 = fluorite$, M = monoclinic, T = tetragonal.

All of the phase diagrams in the A_2O_3 - HfO_2 system except for the second Yb_2O_3 - HfO_2 were generated by the same research group. This has the advantage that it is likely that the same methods and equipment was used for all the studies, making them self consistent and less prone to the inconsistencies shown in the titanate system.

Finally the zirconate system will be considered. In many of these phase diagrams the pyrochlore phase regions are extrapolated but for the purposes of this study which is focused on predicting the phase boundaries this is not an issue. Figure 4.14 shows three different systems in all of which the pyrochlore phase is stable. There are 2 versions of the $Sm_2O_3 - ZrO_2$, both of which imply the pyrochlore forms by an order- disorder transformation but they disagree as to the temperature at which the transformation occurs.



Figure 4.14: Phase diagrams of A_2O_3 - ZrO_2 systems with large A^{3+} cations, A = Eu, Gd, and Sm. Reproduced from [179–181]. T = tetragonal, $C_1 =$ cubic ZrO_2 , P = Pyrochlore, $C_2 =$ cubic Sm_2O_3 , A = A-rare earth, B = B-rare earth, H = hexagonal.

One of the more studied zirconate systems is that for the La_2O_3 - ZrO_2 system and several examples are shown in figure 4.15. In contrast to the zirconate pyrochlores with small A cations (and similarly the hafnate pyrochlores) the pyrochlore phase forms directly from the liquid although the various authors disagree at what temperature this occurs.



Figure 4.15: Several versions of the La_2O_3 - ZrO_2 phase diagram. Reproduced from [180–183].

Figure 4.16 shows 2 strikingly different phase diagrams for the $Nd_2O_3 - ZrO_2$ system. One of these predicts the pyrochlore as a line compound forming from the melt and the other predicts from an order-disorder transformation. However, they both agree that the pyrochlore phase should exist for this combination of elements.



Figure 4.16: Two versions of the Nd_2O_3 - ZrO_2 phase diagram. Reproduced from [180, 182, 183]. T = tetragonal, C_1 = cubic ZrO_2 , c_2 = cubic Nd_2O_3 , P = pyrochlore, A = A-rare earth, H = hexagonal.

More recently there has been work to calculate phase diagrams using thermodynamic modelling. Results from 2 groups are shown in figure 4.17. Yokokawa *et al.* produced phase diagrams for both the La₂O₃ - ZrO₂ and Y₂O₃ - ZrO₂ systems whereas Chen *et al.* (lower figure) concentrated on just the Y₂O₃ - ZrO₂ system. Comparing the 2 theoretical phase diagrams for the yttria system in this figure, a high degree of similarity is apparent. Both predict that no pyrochlore phase forms but that a Y₄Zr₃O₁₂ δ -phase forms at about 1600 K. This is in agreement with the work of Lopato *et al.* [160] who produced δ -phase zirconates for A cations ranging from Sc to Y but not including Dy. Both phase diagrams concur that this is a solid state order-disorder transformation from the fluorite phase.

Comparing the theoretical La_2O_3 - ZrO_2 results with the experimental diagram shown earlier in figure 4.15, it can be seen that the pyrochlore phase exists and that it forms directly from the melt in both cases but some of the details differ. The theoretical study predicts a line compound and the experimental study shows quite extensive solid solution.

The Y₂O₃ - ZrO₂ system has received enormous attention due to the use of Yttria-Stabilised-Zirconia (YSZ) as an oxygen ion conducting electrolyte for solid oxide fuel cells and oxygen sensors [159]. Figure 4.18 shows several experimental phase diagrams of this system which can also be compared with the theoretical systems in figure 4.17. By comparing all of these phase diagrams it is most probable that the phase diagrams produced by Stubican *et al.* [185,185] are the most reliable as the others miss formation concerning the δ -phase compound Y₄Zr₃O₁₂ which has been shown to form by several independent groups [158–160]. It is as important to note that while the other phase diagrams do not predict a δ -phase compound, they also do not predict a pyrochlore and instead just have a region of disordered fluorite solid solution. It is likely, therefore, that this is the first stable δ -phase in the series.



Figure 4.17: Calculated $\rm ZrO_2$ - $\rm A_2O_3$ phase diagrams. Reproduced from [159, 184].



Figure 4.18: Four versions of the $ZrO_2 - Y_2O_3$ phase diagram. Top two reproduced from [186] and [187] respectively and [188, 189] and [185, 190] for the bottom two.

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Structural Studies

While only a limited range of phase diagrams in the $A_2O_3 - BO_2$ system have been generated, there is a much wider range of structural data based on X-ray and neutron diffraction studies. A summary of compounds that form in each system will be given here along with the references where that data can be found. This will be presented in the form of a composition map. A point indicates that a material has been synthesized with that composition and the colour will show which phase(s) have been observed and the source of the information. Much of the non pyrochlore data was located using the online Inorganic Crystal Structures Database (ICSD) [191].

The structural data extends the information on pyrochlore stability, providing information mainly on the titanate, ruthenate and stannate systems (see figure 4.19, red points). By including data from Subramanian (yellow points in figure 4.19) [135] it is nearly possible to completely define the pyrochlore stability field although gaps and uncertainties still exist. It should be noted that of the plumbate pyrochlores, only La₂Pb₂O₇ has been found to form at atmospheric pressure while the others were formed by Sleight [192] at a pressure of 3 kbar at 700 °C. It should also be noted that some of the zirconate pyrochlore and δ -phases have also been formed in a disordered fluorite system. It is the aim of this work to resolve these uncertainties.



Figure 4.19: A phase map constructed from literature studies. Key: Black: Monoclinic P2₁ structure, Red: Cubic Fd $\bar{3}$ m pyrochlore structure from structural studies [193–211], Yellow: Cubic Fd $\bar{3}$ m pyrochlore structure from Subramanian [135] Cyan: Rhombohedral R $\bar{3}$ δ -phase from structural data [1,156,160,212–214], Grey: Disordered fluorite Fm $\bar{3}$ m from structural data [215–218], combinations indicate it has been found in more than one phase or location and an empty box indicates that it has been found as pyrochlore in structural work and the Subramanian review [135] and as a disordered fluorite phase.

4.2.3 Theoretical Studies

There have been several attempts to model pyrochlore compounds on a scale similar to this work. These include work by Minervini et al. [112] who examined the relationship between the oxygen positional parameter and disorder. In this work Minervini *et al.* set out to develop a set of interatomic potentials based on a partial charge model to successfully reproduce the experimentally measured x parameter for a wide range of pyrochlore compounds. They were able to reproduce these values with a high degree of success but in order to reproduce experimental values for the x parameter a varying degree of disorder was required. Without this disorder, the x parameters predicted in this study were systematically low and previous work by Wuensch et al. [219] had found that while the lattice parameters (to which the potentials in this study were fitted) were not significantly increased by small amounts of disorder, the x parameter was influenced in a much more significant way. A defect cluster containing a cation antisite and an oxygen Frenkel pair was used to simulate disorder and the defect energy of this was used to predict the amount of disorder for each composition. The greatest amount of disorder was found in the pyrochlores with small A cations and large B cations. These potentials were used as a starting point for this study.

Stanek *et al.* [220] attempted to model the extent of non-stoichiometry in the pyrochlore systems and how it varies over the wide compositional range. They achieved this by modelling different solution mechanisms that simulated the various ways that the structure can accept excess A_2O_3 or BO_2 and calculating the solution energies of the process. The mechanisms for BO_2 excess considered B cation substitution on to the A cation lattice with charge compensation via A cation vacancies, B cation vacancies and compensation via oxygen interstitials. The mechanisms for A_2O_3 excess considered A cation substitution onto B sites with charge compensation via oxygen vacancies, A interstitials and B interstitials. They found that the most favourable mechanisms for BO₂ excess (for regions where the pyrochlore is stable) involved compensation via A cation vacancies and that for excess A_2O_3 involved compensation via oxygen vacancies. The Kroger-Vink notation [5] for these two mechanisms is given in equations 4.1 and 4.2.

$$7BO_2 + 4A_A^{\times} \to 3B_A^{\bullet} + V_A^{'''} + 2A_2B_2O_7 \tag{4.1}$$

$$2A_2O_3 + 2B_B^* + O_O^* \to 2A_B' + V_O^{\bullet\bullet} + A_2B_2O_7 \tag{4.2}$$

This was an unexpected result as it was generally assumed that pyrochlore would behave like a fluorite (in which BO_2 excess is compensated for by oxygen interstitials) as it had been considered to be simply an oxygen deficient ordered fluorite. In the region very close to the pyrochlore to fluorite transition, Stanek *et al.* [220] found that the preference indeed changes to oxygen interstitial compensation. They went on to postulate that there should be some non-stoichiometry in the titanate system although it may take some time for equilibrium to be reached as cation migration is required for this to occur (cation migration is much slower than anion migration in fluorite related systems).

The variation in activation energies for oxygen migration in the pyrochlore system was modelled by Pirzada *et al.* [221]. In this work they found that the lowest energy migration path for oxygen ions was via an oxygen vacancy (48f) mechanism. In the pyrochlore system this vacancy can "split" [222] for certain compositions. This involves another 48f oxygen adjacent to the vacancy relaxing towards the 8a site forming a cluster of two oxygen vacancies with an oxygen interstitial in between them. This is oriented along a <110>direction (the oxygen interstitial does not occupy the 8a site) and tends to occur for a small number of stable pyrochlores near the pyrochlore - fluorite transition. Migration calculations were performed for both these situations (split vacancies and normal vacancies). For the majority of pyrochlores where the oxygen vacancy it not split, the migration path is a simple <100> type hopping process. For the compositions where the oxygen vacancy does split, the situation is more complicated and details can be found in [221]. The energies were found to agree with the limited experimental data available and the trends show that, in general, the activation energy for oxygen migration decreases rapidly with increasing B cation radius showing little A site dependence until the zirconate pyrochlores are reached. At this point, decreasing A cation radius has a significant reducing effect on the activation energy, although, this may have something to do with the changeover from a symmetrical to a split vacancy starting with $Pr_2Zr_2O_7$.

Minervini *et al.* looked in detail at the disorder processes that occur in pyrochlores [223]. They found that by plotting the formation energy of a clustered cation antisite pair and an oxygen Frenkel pair (a 48f oxygen vacancy and an oxygen interstitial on the 8a site) as a contour map that the 2.8eV contour accurately reproduced the boundary of the pyrochlore phase stability region (see figure 4.20). The authors stated that while this value may seem to be large at first, they used a full ionic model which tends to overestimate



Figure 4.20: Contour Map of the defect formation energy for an anion Frenkel adjacent to a cation antisite pair. Reproduced from Minervini *et al.* [223].

the disorder enthalpy. It should be noted that the δ -phase was not considered in this study. Panero *et al.* [224] have also looked at intrinsic defects in pyrochlores from a first principals approach. They showed that cation antisite defects reduce the energy for the formation of an oxygen Frenkel pair and went on to suggest that the disordering process was driven by the presence of cation disorder since the formation of an oxygen Frenkel pair in a fully ordered system has a much greater energy. They also found that the zirconate pyrochlores show a much greater degree of disorder but they predict that defect formation in the stannate pyrochlores is more like the titanates than other theoretical studies have predicted. They explain this by pointing out that Sn - O bonding is more covalent than that for Ti or Zr and that bonding type as well as ionic radii is also a factor.

Stanek and Grimes [225] used the cation antisite and oxygen Frenkel pair

cluster used by Minervini [223] to simulate the disordering process in pyrochlore and hence calculate the order - disorder temperatures for the Hafnate pyrochlores. This was achieved by plotting the logarithm of the defect energy against 1/T where T is the transition temperature for experimentally determined compounds. A linear fit was calculated and then predicted temperatures were obtained. Rushton *et al.* [226] recently extended this work to include the zirconate pyrochlores and a graph from this work, showing the transition temperatures for the hafnates and the zirconates is reproduced in figure 4.21.



Figure 4.21: Pyrochlore to defect fluorite transition temperatures for zirconate and hafnate pyrochlores squares indicate experimental disorder temperatures and circles indicate predicted values. Reproduced from [226].

There have been several other studies to examine specific pyrochlore compositions rather then predicting trends across the entire range. Wilde and Catlow [227] looked at diffusion and defects in $A_2B_2O_7$ with A and B consisting of Gd, Y and Zr, Ti respectively. Their results indicate that diffusion is effected by hopping between 48f sites and that these compounds exhibit high solubility for divalent cations such as Ca and Sr. The same authors also performed a molecular dynamics study on $Gd_2Zr_2O_7$ to look into the oxygen ion mobility [228]. They found that once again disorder is very important in this system, in the perfectly ordered system there was very little migration but by introducing some disorder to the system oxygen could be induced to diffuse through the system.

As mentioned earlier there have been very few theoretical studies on the δ phase. Of note, however, is the work by Bogicevic *et al.* [157, 158] on the ordering of the ions in this structure. These authors considered yttria [158] and scandia [157] stabilised zirconia. They identified 104 possible configurations for ordering 7 cations in an fcc cell (as per the fluorite structure). Only two of these were determined to have rhombohedral cell vectors. For these two systems the oxygen ions were then added as they would be in the fluorite system and all the symmetrically distinct ways of removing two oxygen ions were considered in order to yield the Y₄Zr₃O₁₂ stoichiometry. This yielded 45 possible systems which were then subject to energy minimisation to find the lowest energy configuration. This study was based on the first principals using the VASP code. VASP (Vienna Ab-initio Simulation Package) is a package for performing ab-initio quantum-mechanical molecular dynamics (MD) using pseudopotentials and a plane wave basis set [229].

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4.3 Methodology

In order to determine the phase composition regions and their limits it was decided to use the data from Minervini et al. [223] to model the pyrochlore to disordered fluorite transition. This was chose because, as mentioned in section 4.2.3, this agreed with the available experimental data. This leaves 2 transitions to consider, as show in mechanisms 4.3 and 4.4. In these mechanisms the compound (e.g. $A_2B_2O_7$) represents the lattice energy of the indicated system. If the reaction energy is negative it means that the transition is energetically favourable. Clearly this is a very simple approach which assumes that the internal energy change (given by the energy minimisation approach) is completely dominant over, for example, vibrational energy terms. Although it is desirable to employ a free energy minimisation approach, a code capable of performing this type of calculation was not obtainable at the time (see further work section for more discussion and later in this chapter). Also, the aim here is to provide an approximate map or guide to the overall phase composition relationships which rely on trends rather than absolute energy values.

$$A_2 B_2 O_7 \rightarrow A_4 B_3 O_{12} + BO_2 \tag{4.3}$$

$$A_2B_2O_7(\text{cubic}) \to A_2B_2O_7(\text{monoclinic})$$
 (4.4)

Partial charge potentials were derived as described in chapter 3, using the potentials from Minervini *et al.* [112] as a starting point. These original potentials were adapted in order to reproduce as closely as possible the exper-

Table 4.4: Percentage volume changes with respect to experimental data using the short range interatomic potentials from table 4.5. Volume changes in black were fitted to the pyrochlore structure, those in red were fitted to the delta phase and blue indicates monoclinic. Those which are blank indicate either a disordered fluorite forms experimentally for that composition or there was no experimental data to fit to. Averages do not include monoclinic data.

	Ti	Ru	Mo	Sn	Hf	Zr	Pb	Average
La	4.99			0.20	-0.87	-0.49	-0.35	-0.22
Pr	4.78			0.31	-1.77	-0.60	-0.20	-0.52
Nd	4.31	-0.46		0.15	-0.51	-0.67	-0.44	-0.46
Sm	0.21	-0.40	-0.40	0.55	-0.25	0.35	0.13	0.03
Eu	0.65	-0.31	0.03	0.60	0.18	1.15	0.26	0.37
Gd	0.47	-0.01	0.56	0.78	0.35	1.12	0.50	0.54
Tb	0.25	-0.39	0.66	0.60	0.40			0.28
Dy	0.25	-0.33	0.89	0.53	0.47			0.34
Y	0.42	-0.20	0.94	0.60	0.40	-0.83		0.22
Но	0.31	-0.45	0.81	0.56	0.71	-0.54		0.23
Er	0.04	-0.10	1.16	0.60	-0.70	-0.13		0.15
Yb	0.56	-0.29	1.35	0.69	-0.83	-0.45		0.17
Lu	0.41	-0.62	1.38	0.68	-0.60	-0.42		0.14
In				-0.32				-0.32
Sc	0.53					0.35		0.44
Average	0.32	-0.24	0.30	0.47	-0.23	-0.10	-0.02	

imental unit cell volume of: the pyrochlore compounds, the δ -phase and the simple A₂O₃ and BO₂ oxides (see table 4.4 for the actual volume changes). A shell model was employed for the oxygen ions. Cation shells particularly for zirconium ions had been used in previous studies but caused problems (coreshell separation) in conjunction with small A cation zirconate pyrochlores (that needed to be calculated in order to ascertain the stability of the δ phase in this region). Removing them seemed to have very little impact on either the lattice energy or the unit cell volume.

Once the potentials had been derived the perfect lattice calculations were run

Species	A (eV)	ρ (eV)	C (eV $Å^6$)
$O^{1.7-} \leftrightarrow O^{1.7-}$	4870.00	0.2670	77.00
$La^{2.55+} \leftrightarrow O^{1.7-}$	2306.26	0.3263	23.25
$Pr^{2.55+} \leftrightarrow O^{1.7-}$	2236.02	0.3225	23.94
$\mathrm{Nd}^{2.55+} \leftrightarrow \mathrm{O}^{1.7-}$	2205.88	0.3206	22.59
$\mathrm{Sm}^{2.55+} \leftrightarrow \mathrm{O}^{1.7-}$	2179.20	0.3181	21.49
$\mathrm{Eu}^{2.55+} \leftrightarrow \mathrm{O}^{1.7-}$	2172.45	0.3168	20.59
$\mathrm{Gd}^{2.55+} \leftrightarrow \mathrm{O}^{1.7-}$	2165.40	0.3158	19.90
$\mathrm{Tb}^{2.55+} \leftrightarrow \mathrm{O}^{1.7-}$	2137.47	0.3138	19.25
$Dy^{2.55+} \leftrightarrow O^{1.7-}$	2130.65	0.3121	18.68
$Y^{2.55+} \leftrightarrow O^{1.7-}$	2107.60	0.3109	17.51
$\mathrm{Ho}^{2.55+}\!\leftrightarrow\!\mathrm{O}^{1.7-}$	2113.67	0.3110	18.16
$\mathrm{Er}^{2.55+} \leftrightarrow \mathrm{O}^{1.7-}$	2103.60	0.3097	17.55
$Yb^{2.55+} \leftrightarrow O^{1.7-}$	2075.26	0.3076	16.57
$Lu^{2.55+} \leftrightarrow O^{1.7-}$	2069.99	0.3067	16.87
$\text{In}^{2.55+} \leftrightarrow \text{O}^{1.7-}$	2001.65	0.3016	11.85
$\mathrm{Sc}^{2.55+} \leftrightarrow \mathrm{O}^{1.7-}$	1944.21	0.2960	11.85
$Ti^{3.4+} \leftrightarrow O^{1.7-}$	1865.80	0.2946	0.00
$\mathrm{Ru}^{3.4+} \leftrightarrow \mathrm{O}^{1.7-}$	1883.39	0.2954	0.00
$\mathrm{Mo}^{3.4+} \leftrightarrow \mathrm{O}^{1.7-}$	1901.50	0.3011	0.00
$\mathrm{Sn}^{3.4+} \leftrightarrow \mathrm{O}^{1.7-}$	1945.41	0.3099	13.66
$\mathrm{Zr}^{3.4+} \leftrightarrow \mathrm{O}^{1.7-}$	1953.80	0.3111	5.10
$Pb^{3.4+} \leftrightarrow O^{1.7-}$	2005.10	0.3203	19.50
$Ce^{3.4+} \leftrightarrow O^{1.7-}$	2058.36	0.3292	22.50

Table 4.5: Short range potential parameters used for this study. Harmonic oxygen core-shell parameter k = 32.0.

using the CASCADE code [102] as described in chapter 3. The potentials used are presented in table 4.5.

4.4 **Results and Discussion**

In order to model the hypothetical cubic pyrochlore and δ -phases in the transition regions, the lattice parameters for known systems were extrapolated with respect to A and B cation radii. The systems were then simulated and the resulting lattice energies combined, as per mechanisms 4.3 and 4.4, to calculate the most stable phase.

The initial results were disappointing as it was found that none of the monoclinic phases were stable with respect to the cubic pyrochlore system and only a few of the experimentally confirmed δ -phase compounds were found to be stable (Yb-Sc zirconates and In₄Sn₃O₁₂ but not Sc₄Ti₃O₁₂).

Considering the cubic pyrochlore to monoclinic transition first, it was found that the reaction energies were 0.81 and 1.29 eV per formula unit in favour of the cubic phase for La₂Ti₂O₇ and Nd₂Ti₂O₇ respectively (but these are small with respect to the total lattice energies of -270.47 and -273.03 eV). However it should be noted that the hypothetical cubic phases had final cell volumes (after relaxation) much closer to the predicted ones than the monoclinic phases. The hypothetical cubic phases show volume discrepancies of +0.12% and +0.8% (for Nd₂Ti₂O₇ and La₂Ti₂O₇ respectively) whereas the volume discrepancies after relaxation for the monoclinic phases were +4.31%and +4.99% (for Nd₂Ti₂O₇ and La₂Ti₂O₇). This suggests that these potentials, while sufficient to model a cubic system lack terms that would aid in representing a monoclinic system. It is, nevertheless, impressive that the monoclinic phases are reproduced so well (see table 4.4) and suggests only modest improvements will be necessary (see further work for more information). This seemingly excessive preference for cubic systems may be partly due to the use of centro-symmetric potentials as these almost certainly favour a cubic symmetry over the monoclinic system. A way of getting around this problem would be to use an elliptical breathing shell model [116] for the oxygen and re-derive a potential based on that to fit both the monoclinic phase and the cubic phase equally well, without compromising the δ -phase system too much. Unfortunately neither of the two codes available at the time (CASCADE [102] and GULP [103]) implemented an elliptical breathing shell model so this was unable to be tested and this should be investigated in further work when codes implementing this feature are available.

In order to address the problem regarding the delta phase transition point (initially the calculations only predicted that the Yb-Sc zirconates and $In_4Sn_3O_{12}$ were stable with respect to the pyrochlore structure) it was necessary to reconsider whether the ordered δ -phase structure is what is actually forming in reality. In all experimental systems this system is reported to be completely disordered on the cation sublattice as opposed to what is being simulated here. Modelling the disordered system would require large supercells and a Monte-Carlo type approach. This would have been much more computationally challenging. As a compromise, an approximate configurational entropy contribution (see appendix A for details) to the lattice energy was computed for the cation disorder at order-disorder transition temperature given by Duran and Pascual [167] (i.e. 1600 °C). By including this it was possible to predict much more closely the cubic pyrochlore to δ -phase transition point for the zirconates. Nevertheless, it was found that $Y_4Zr_3O_{12}$ and $Ho_4Zr_3O_{12}$ were still slightly more stable as pyrochlores but that this preference was less than 0.09 eV so these have been included in figure 4.22 as points that have

been confirmed as delta phase compounds. The final phase map is shown in figure 4.22.

The potential model does not yet reproduce the monoclinic phases sufficiently accurately according the criteria used to derive the potentials (deviations in the unit cell volume of > 1.5% were deemed unrepresentative of the real material). Even if they were included, the results predict a result known to be untrue. Due to this, the experimentally determined points have been used to define the phase stability of the diagram. Without further work it is difficult to say for certain what happens in this region and therefore it is suggested that all of the the compounds inside the line in the upper left form non-cubic materials with the $A_2B_2O_7$ stoichiometry. These materials may be monoclinic as per the titanate compounds or something else.

On the other side of the map the boundary between the disordered fluorite and the pyrochlore phase was not explicitly calculated in this study but as mentioned earlier the 2.8 eV contour, taken from Minerlvini *et al.* [223] (see figure 4.20) was used. This predicts that two of the rare earth plumbates previously only observed at high pressure by Sleight [192] may be stable under normal conditions and as such these have been included on the pyrochlore side of the line.

Considering next the δ -phase region, this study predicts 5 new compounds with this structure: Sc₄Ru₃O₁₂, Sc₄Mo₃O₁₂, Sc₄Sn₃O₁₂, Lu₄Sn₃O₁₂, Yb₄Sn₃O₁₂. It also predicts the stability of 3 previously unknown pyrochlore compositions (In₂Ti₂O₇, In₂Ru₂O₇ and In₂Mo₂O₇). Due to the inability to probe the δ phase fluorite transition it is assumed that while the δ -phase is stable with



Figure 4.22: Phase map showing the stability of cubic $A_2B_2O_7$, non cubic $A_2B_2O_7$, disordered fluorite and $A_4B_3O_{12}$ phases at low temperatures. Key: Blue = Non cubic (possibly monoclinic pyrochlore), Yellow = Cubic Pyrochlore forming from the melt, Orange cubic pyrochlore formed by orderdisorder transformation, Black = δ -phase postulated to form from the melt, Light Blue = δ -phase formed by and order-disorder transformation, Red = disordered fluorite, Yellow/Red cubic pyrochlores formed by Sleight under high pressure [192].

respect to the pyrochlore phase for some of the plumbates, since none have been formed experimentally it is prudent to assume that these phases remain as fluorite. Further work is clearly necessary to bring greater understanding and certainty to this region of the phase map.

The central region of figure 4.22 is the most complex area and technically interesting region. In this region the pyrochlore and δ -phases have been given 2 colours depending on how they are predicted to form. Pyrochlores in orange were previously identified by Stanek *et al.* [230] and Rushton *et al.* [226] to

undergo a solid state pyrochlore to fluorite order-disorder transformation and in agreement with the phase diagrams the temperature at which this occurs increases with A cation radius. By carefully examining the phase diagrams dealing with the larger A cation hafnate pyrochlores it was decided to draw the line for this upper boundary between Eu₂Hf₂O₇ and Sm₂Hf₂O₇. This was then extended to ensure the pyrochlore phase region included the two plumbate pyrochlores and this extension also included La₂Ce₂O₇. In their phase diagram of the Yb₂O₃ - HfO₂ system, Duran and Pascual [167] show Yb₄Hf₃O₁₂ forms via an ordering process from the fluorite phase, analogous to that observed with the pyrochlores. It is therefore suggested that like the pyrochlore system, this transition temperature will rise the further away from the pyrochlore to δ -phase boundary (i.e. decreasing A cation radius) until the phase is stable up to the melting point. A tentatively boundary has been marked for this transition but there is no way of determining this from the results presented here.

Many of the materials that have been found to show high resistance to radiation damage tend to appear in the centre of this diagram, close to the pyrochlore to fluorite or pyrochlore to δ -phase boundary. All of the systems in this region demonstrate a large degree of intrinsic disorder and as such the disordering processes caused by atomic displacements have little overall effect. The material examined by Sickafus *et al.* [131, 132] (Er₂Zr₂O₇) is actually on the border of all three phases and this suggests that the δ -phase compound with the same cations (if processing conditions allow it to form from the fluorite) may also be worth studying as would other materials in this region such as Er₄Hf₃O₁₂ and Lu₄Zr₃O₁₂. Compositions in this region are also the ones that exhibit the greatest degree of non-stoichiometry.

Figure 4.23 shows the expected stability for these compounds at high temperatures (e.g. 2000 K). At such temperatures the pyrochlore and δ -phases that undergo an order-disorder transition have become fluorite. This is also the expected phase after extensive radiation damage as preliminary work on Yb₄Zr₃O₁₂ by Sickafus and Valdez [231] has shown. In this most recent work, Sickafus and Valdez carried out "ion beam" irradiation studies and found that under "high doses", this material is transformed back to the fluorite phase.



B Cation Radius (Å)

Figure 4.23: Phase map showing the stability of cubic $A_2B_2O_7$, non cubic $A_2B_2O_7$, disordered fluorite and $A_4B_3O_{12}$ phases at high temperatures. Key: Blue = Non cubic (possibly monoclinic pyrochlore), Yellow = Cubic Pyrochlore, Black = δ -phase, Red = disordered fluorite, Yellow/Red cubic pyrochlores formed by Sleight at 300 Kbar [192].

4.5 Conclusions

Phase maps have been produced to provide a general understanding of the relative stability of the pyrochlore, δ -phase and disordered fluorite systems as a function of composition using a combination of atomistic simulation and experimental data. A set of potentials has been derived that almost perfectly reproduce both the cubic pyrochlore to δ -phase transition and the structures of both compounds. Further work needs to be performed to develop a potential set to model correctly the cubic pyrochlore to monoclinic transition.

Further work, including both simulation and experimental work needs to be done with the plumbates and the cerates to identify which phases form with these combinations of cations as the projected fluorite field here is essentially an assumption based on limited experimental data.