Chapter 7

Concluding Comments and Future Work

> *"There always remain in the abyss of things slumbering, parts which have yet to be awakened."*
>
> *- Gottfried Wilhelm von Leibniz*
> *On the Ultimate Origination of Things, 1697*

7.1 Summary

The last four chapters have attempted to solve problems, all of which involve disorder in ceramic systems. In particular, each of these chapters dealt with a specific technological issue, the detailed conclusions of which are included in each chapter. It is therefore not the purpose of this chapter to repeat those results. However, what has not yet been provided is the connection between each chapter and their general relation to disorder.

Firstly, all of the systems considered in this thesis involve fluorite or fluorite related oxides, namely UO_2, ZrO_2 and $A_2B_2O_7$. Furthermore, each chapter dealt with some aspect of structural disorder in one of these systems. In Chapter 6, intrinsic disorder was considered in the $A_2B_2O_7$ group of materials. The calculation of defect energies led to a prediction of yet unobserved compounds, namely $Dy_2Hf_2O_7$, $Ho_2Hf_2O_7$ and $Er_2Hf_2O_7$. This was facilitated by relating the fluorite to pyrochlore disorder transformation temperature to a local disorder process. Chapter 5 considered non-stoichiometry in the same series of compounds, broadening the scope to consider a form of extrinsic disorder that does not involve species foreign to the lattice constituents (recalling the comments from Chapter 1, classifying only thermally activated disorder as intrinsic, though it is acknowledged that non-stoichiometry is at times referred to as intrinsic). Chapter 3 considered the solution of fission products, especially Kr, thereby further expanding the types of disorder considered to include a species different than that of the lattice ions (and therefore clearly extrinsic). In each of these three chapters, each system was modelled as an infinite single crystal.

However, real materials have surfaces and it is important to acknowledge that with respect to an infinite crystal, surfaces are defects (it is noted that grain boundaries are another form of termination, though not considered in this work). Surfaces were included in Chapter 4, through the calculation of segregation energies. The segregation studies show quite clearly how strong the influence of surface structure can be on defect behaviour. That is, the defect energies change dramatically increasing or decreasing in stability as they approach a specific surface.

This thesis is not an exhaustive study of disorder in fluorite and fluorite related oxides. Rather, it is a selective representation of important concepts. In many cases, the models were forced to make use of approximations on account of the complexity of the problems encountered. As computing resources continue to improve, these approximations will either become unnecessary or at least less significant (e.g. as the size of the repeat units can be increased further). Although much information has been presented in this thesis, there is still even more work needed in order to better understand disorder and all of its manifestations in these materials. Some possibilities for further work are discussed in the following section.

7.2 Future Work

7.2.1 Bulk Related Studies

- Figure 4.4 described the binding energy between a divalent ion and a charge compensating oxygen vacancy as a function of distance between these two species. This plot showed that at rather large separations (i.e. ≈10Å), the binding energy is still ≈25% of its maximum value. This result suggests that the idea of a completely isolated defect is only valid at dopant levels below 0.1%. An improved Debye-Hückel correction should be developed to better describe defect - defect interaction.

- The material systems modelled in this work have the advantage (from the pair potential point of view) of being highly ionic. As noted in Chapter 3, high quality quantum mechanical calculations are accepted as a more accurate representation, in terms of electronic contributions. Currently, QM calculations are limited by the number of atoms that can be realistically considered. As computing resources improve, QM type calculations will become more feasible, as more atoms will be able to be modelled.

- Contour maps can be used predictively to consider elements which have not been explicitly modelled, but whose ionic radii are known. This may also include certain compounds whose elements that are able to exhibit variable charge states (e.g. Pr and Ce containing). However, the consideration of elements with variable charge state requires comparison to ternary phase diagrams. This problem becomes even more complicated if the charge state varies with temperature, which would then introduce another variable- the partial pressure of oxygen.

- In order to validate the prediction of $Dy_2Hf_2O_7$ formation (as discussed in Chapter 6), experimental verification is necessary. It is the belief of the author that precision calorimetry experiments will yield results supporting the predictions described in Chapter 6. However, it is also acknowledged that experiments of this type are difficult. As previously mentioned, there are two cation sublattices in the pyrochlore structure. If there is ordering of these cationic sublattices, it will take long periods of time to reach equilibrium. Also, there may be deviations from stoichiometry if the sample reacts with the gas phase.

7.2.2 Surface Related Studies

- The segregation of fission products to surfaces of UO_2 was a more complicated problem than initially expected. With improved computing resources, the remaining calculations can be completed in order to formulate a systematic statement regarding the segregation of these fission products in this system.
- In addition to free surfaces, the segregation of fission products to grain boundaries in UO_2 is significant. In a similar fashion to the model used in Chapter 5 to simulate segregation to free surfaces, it is possible to model segregation

to grain boundaries. However, it is noted that these calculations will be even more intensive than those considering only free surfaces. Instead of considering a single simulation cell, grain boundary calculations require another cell of a specific orientation placed on top of the original cell. This significantly increases the number of atoms which need to be considered.

- Oxygen vacancy diffusion can be calculated in UO_2, CeO_2 or ZrO_2, as it is an important phenomenon in all of these materials. Vacancy migration was not originally considered because of code limitations, namely the lack of ability to simulate charged defects. However, a methodology has been formulated which will allow us to circumvent the problem. First, a defect cluster such as $\{(\mathrm{Ba}_{\mathrm{U}})'' {:} (\mathrm{V}_{\mathrm{O}})^{\cdot\cdot}\}$ is introduced near to the bottom of the repeat unit, as far from the surface as possible. The cation is then pinned whilst moving the oxygen vacancy towards the surface. The binding energy of the oxygen vacancy to the barrier defect can be calculated independently, and subsequently subtracted from the clustered defect energy at each corresponding oxygen vacancy step. Therefore, the only energy of interest is that of the oxygen vacancy nearing the surface. The binding energy correction term is determined by performing a similar calculation with the repeat unit mirrored at the surface in order to account only for bulk effects. This correction assumes that the $(\mathrm{Ba}_{\mathrm{U}})''$ defect pinned in the bulk does not alter the phenomenon at the surface significantly and needs to be examined more closely. In this case, a code such as CHAOS [74] might be more useful in that it treats Region II as a dielectric continuum.

- This thesis has not taken into account space charge effects. This effect is noted to be of importance, but unfortunately, there was not enough time to take it into consideration. The formation of electrically active surfaces and grain boundaries via this effect is thought to be especially important.

- In Chapter 4, the limitations of the MARVIN code were discussed. In addition to region size issues, the issue of Region II polarizability was mentioned. Clearly, modifications to the code in order to include Region II polarizability are necessary. This could take the form of a single continuum approximation (e.g. analogous to the Mott-Littleton Region IIb approach), or a layer by layer calculation where ions are dispersed (e.g. more like the Mott-Littleton Region IIa).

- At this point, the surfaces of pyrochlores have yet to be investigated. If these materials are to be used as nuclear waste forms, then surface related phenomena (such as dissolution) is important. Initially, morphology and hydroxylation calculations are possible, as these calculations have already been performed on similar materials, such as UO_2 [46, 259]. The simulation of radiation damage is also of interest. This might require molecular dynamics in order to simulate the instantaneous amount of energy which needs to be transferred to an ion during irradiation.