Chapter 7

Further Work

7.1 Fluorite Related Phases

7.1.1 Pyrochlore

The primary aim of any further work in relation to this topic will be to develop a potential model, most probably using elliptical breathing shells, in order to accurately model the monoclinic to cubic pyrochlore transition. It may be advisable to attempt a more rigorous modelling approach using quantum mechanical techniques similar to those of Bogicevic *et al.* [158] to gain information with which to fit the breathing shell parameters since no elastic constant data for the monoclinic phase is available in the literature. Once this model has been developed, it can then be used to extend this work to the large A small B cation region of compositional space where the current model fails.

7.1.2 Disorder Processes Resulting in Fluorite

Calculations should also be performed to probe the pyrochlore and δ-phase to disordered fluorite compositional boundary. Following on from the work of Chartier *et al.* [266] who used molecular dynamics to simulate a disordered fluorite system, it may be possible to use this technique to gain further insight into these materials. It may also be possible to use MD to examine disordered versions of the δ-phase in order to directly calculate this instead of relying on the configurational entropy term as at present. Failing this a Monte-Carlo method could be used on a large supercell of the δ-phase to model the disorder process at this composition.

7.1.3 Amorphisation of the δ-phase

Since the δ-phase has been shown to have a very high resistance to amorphisation [231], simulations should be carried out to increase our understanding of this system. This should start with a calculations to determine the intrinsic defects as this will allow a preliminary ordering of the amorphisation resistance. It should also be possible to use molecular dynamics to study the effect of α-recoil collision cascades in order to understand why this system is resistant to amorphisation. It will facilitate comparison with the pyrochlore and fluorite and allow the related structures to be ranked by their amorphisation resistance. These simulations would confirm whether the δ-phase does amorphise or if it transforms to fluorite and identify defect clusters that may form during this process. The transformation process may be difficult to simulate with MD as it involves a rhombohedral to cubic conversion and undoubtedly a volume change and up to this point all simulations have been carried out under constant volume conditions. The reverse of this process could be simulated by quenching from a melt, or Monte-Carlo techniques could be used to disorder the system before it is relaxed under a constant pressure regime.

7.2 Accommodation of Actinides

7.2.1 Pyrochlore

Assuming a model that can accurately simulate the monoclinic phases is developed, solution processes should be extended to cover these materials. Potentials can be developed to model americium and some of the other minor actinides, which are also long lived, in order to predict their solution properties in these materials. Following the suggestion of Fortner *et al.* [30] a U^{5+} potential should be developed and solution incorporating this should be examined.

The calcium compensated systems should be extended to compare the solution properties in the related zirconolite and betafite systems. And both experimental and simulation work should be carried out with the aim of examining the phase equilibria of these related systems. With this in mind, a similar study to that of Chapter 4 could be performed.

7.2.2 δ-Phase

If this very amorphisation resistant material is to be used as a waste form, it must be able to accommodate high concentrations of actinides and fission product ions. It should easily be possible to produce a set of simulations modeling the solution of these species in a similar manner to that done for the pyroclores in Chapter 5.

7.3 Doped MgO

7.3.1 Anisotropy

In order to identify whether the conclusions regarding the reduction in anisotropic behaviour of collision cascades in impure MgO are valid, a more detailed study should be performed examining the same set of directions with the same defect concentration but varying the defect distribution in the simulation cell. This is essential as a single cell is really only one defect configuration and the change in anisotropy may be specific to that configuration. In order to be sure of these conclusions an average over many configurations is required. Different dopants, such as Li^+ ions, should be considered to see if the same trapping effect is observed for oxygen interstitial ions at the oxygen vacancies (introduced to charge compensate for Li^+ substitutional cations). It would also be possible to simultaneously dope both Al^{3+} and Li^+ into the lattice. In this case the Li^+ and Al^{3+} substitutional cations are self compensating and thus no potentially trapping vacant sites are introduced into the lattice.

7.3.2 Long Timescale Processes

Accelerated dynamics techniques should be used to analyse some of the defect clusters found at the end of the conventional dynamics simulations taking into account the impurity ions in the lattice in order to see how impurities effect the long timescale affects of radiation damage in real materials. The conventional dynamics simulations should also be extended to consider larger systems so that more energetic PKA energies can be investigated. As the PKA impulse increases, the more impurity ions the cascade will encounter, making any small timescale effects that the impurity ions have on the cascade more apparent.

7.3.3 Analysis of the Cascades

Determining the cascade size by measuring the distance between the furthest two defects in the cascade is very simplistic. A better way to model this would be a cascade volume calculation. This would require the construction of a mesh encasing the outer cascade generated defects. While this sounds simple, the difficulty with this method originates from distinguishing between intrinsic defects and cascade generated defects.

MgO was chosen as an example of a simple material with the hope that the results would be clearly identifiable. The results turned out to be unexpectedly complex and far from simple to interpret. Nevertheless, further work should also consider prospective wasteform materials to find out if the the effects seen in MgO are typical for all systems. An intermediate step in this direction would be to repeat this work with $MgAl_2O_4$ (spinel).