Chapter 1

Introduction

The long term storage and eventual disposal of radioactive waste is a major concern at the current time. In the U.K. solutions to this problem become even more important as, in order to keep our commitment to the Kyoto accord [2] and maintain current energy production, the Government is seriously considering the possibility of building a new generation of nuclear power plants. Uncertainties regarding nuclear waste disposal are likely to be a major hurdle to public acceptance of new nuclear build.

Adding to the radioactive waste stockpile is the highly enriched uranium and plutonium that has been released from the dismantling of nuclear warheads under the strategic arms reduction treaties between the U.S.A. and Russia. This legacy material needs to be stored and disposed of in a form that ensures it cannot be used again in a weapons program.

Current strategy for the disposal of both civilian and military waste involves immobilising in glass, pouring the molten glass into a container and then disposal in a deep geological repository. A future improvement to this would be to immobilise the material in a ceramic and encapsulate this in a steel container before deep disposal. Pyrochlore ceramics have been considered for this application and discussion regarding the use of these and other fluorite related materials as waste forms for radionuclides has been discussed (literature details are given at the beginning of Chapter 5). The particular ability of pyrochlore compounds to accommodate uranium and plutonium has been considered in depth in this thesis.

Before the specifics regarding nuclear waste are discussed it is important to understand the background issues as to what exactly the problem is in the first place and why it is likely to become even more acute in future. This and previous work on wasteform materials for nuclear waste will be discussed in Chapter 2. Chapter 3 describes how the simulation software operates in order to provide an understanding of the limitations and advantages of these techniques. The next chapter (Chapter 4) aims to give greater insight into into three fluorite related phases. In this chapter, the stability of minerals which form in either the pyrochlore structure, the δ-phase or fluorite solid solutions are analysed with respect to composition. All of these materials have been found to be remarkably resistant to amorphisation and as such are interesting candidate phases for a nuclear wasteform. Chapter 5 (incorporating work published in [3]) focuses on the pyrochlore materials previously discussed in Chapter 4. The aim of the work in this chapter is to simulate various solution processes for uranium and plutonium and develop trends in order to predict which pyrochlore composition can accommodate the highest concentration of these dangerous species. Chapter 6 (incorporating work to be published in [4]) moves away from fluorite related materials to a much simpler material, MgO. The aim of this study is, using molecular dynamics, to gain insights into how materials react to decay events. The normal scope of molecular dynamics simulations is extended slightly by incorporating a small concentration of impurity ions into the material in order to more accurately model a real wasteform material and these results are compared to simulations performed in a pure lattice to see if there are any systematic changes. Finally suggestions for further work are given in Chapter 7.

Lesser contributions to collaborative work have also been made and copies of these papers can be found in Appendix C.

1.1 Kröger-Vink Notation

Kröger and Vink proposed a notation to describe point defect chemical reactions [5]. The point defects are assumed to be dilute species, with the solid being the solvent. The nomenclature consists of three parts; the body, the superscript and the subscript. The body represents the defect itself, ie. V for a vacancy or Mg for a magnesium ion. The superscript represents the effective charge of the defect i.e. a magnesium vacancy has an effective charge of $^{2-}$. A positive charge is represented by a dot ($^{\bullet}$) and a negative charge by a prime ($'$) and neutral by ($^{\times}$). The subscript represents the site of the defect or if it is an interstitial, ($_i$), ($_{Mg}$) would represent a magnesium lattice site. Several examples in the MgO system follow:

Mg Vacancy

V''_{Mg}

A Mg ion has a charge of $^{2+}$ therefore its absence implies a net charge in the lattice of $^{2-}$.

Mg Interstitial

$Mg_i^{\bullet\bullet}$

As the previous example except this time there is an extra Mg ion in the lattice so the effective charge is $^{2+}$

Ba^{2+} substitutional on Mg site

$Ba^{\times}_{Mg}$

Ba^{2+} has the same charge as Mg^{2+} so the lattice remains neutral.