Chapter 1

Introduction

Atomic scale computer simulation techniques have been used to predict the crystal structure and defect properties of a series of ceramic materials. The techniques incorporate energy minimization and equivalent procedures to relax ion positions subject to interatomic forces. Application has been made to a number of related solid state systems.

Initial investigation was made to the crystal structure of perovskite materials. Crystal structure predictions are an essential precursor to a more in depth study of the perovskite compounds. Since there is a multitude of compositions that are possible when one considers that the A cations are able to adopt 1+, 2+ and 3+ valence states, B cations are able to adopt 5+, 4+ and 3+ valence states, and the anion need not be oxygen, some limitations need to be imposed to make a viable study. Here, the two cations were restricted to being trivalent, and the anion to be oxygen, further to this, the large A cation was limited to be a rare earth ion. Once structural determinations were made, further work was conducted on more application specific

considerations.

The problem of adequately dealing with High-Level Nuclear waste (HLW) is escalating, and pressure from environmental organisations is increasing the importance of the issue on the global political scene. Previous studies [4, 5] that considered pyrochlore ceramics as possible encapsulation materials have shown that assessing the structural stability of complex oxides is a suitable method in determining the applicability for HLW storage. Here, perovskites were investigated using a similar approach. That is, atomistic computer modelling techniques have been employed to examine several possible candidate materials. As such, the radiation damage of an extensive range of perovskite oxides were investigated for their suitability to be incorporated in nuclear waste forms via a consideration of the intrinsic defect processes. These results were then compared to the previous work on a series of pyrochlore materials. This leads to a series of propositions concerning the relative radiation tolerance of perovskite to pyrochlore oxides.

With dwindling fossil fuel reserves and increasing awareness of global warming attention is being directed towards renewable and non-polluting energy systems. The Kyoto protocol was created to set targets for industrialised nations to cut their greenhouse gas emissions. As part of this drive for a non-polluting, energy efficient system, solid oxide fuel cells (SOFCs) are being rigorously investigated. Maintaining the energy theme, the suitability of a subset of the perovskite oxides was assessed for their application to solid oxide fuel cell (SOFC) components. This required consideration of the defect behaviour of the materials when doped and an investigation into the compensation mechanisms operating when divalent cations were introduced into the materials.

The same approach used for the perovskite materials has then been translated to

the dielectric behaviour of doped zinc fluoride. The lithium doping of zinc fluoride has been shown experimentally to exhibit an anisotropic dielectric relaxation. The mechanism of this was previously a matter of contention, however, through atomistic simulations it has been possible to develop a defect model that is able to describe this anisotropy.

This thesis encompasses a variety of different solid state issues, all linked through a central theme which emphasises the importance of atomic scale defect processes in inorganic materials, and their interaction with different crystal structures. The structure of this thesis allows each issue to be viewed as a separate, self-contained chapter, incorporating a literature review, a presentation of the results obtained from simulation studies, and a critical discussion with summary conclusions.

This Introduction (Chapter 1) sets the scene for the thesis by establishing the themes, aims and objectives of the research, and describes the layout of the following chapters. The methodology used throughout the research is detailed in Chapter 2, preceding four self-contained chapters concerning pertinent solid state issues. Firstly, the perfect lattice is presented and discussed in Chapter 3, followed by the questioning of the suitability of perovskites as radioactive hosts in Chapter 4. Chapter 5 discusses extrinsic defect reactions and the application of perovskites to SOFC technology, while Chapter 6 investigates the anisotropic dielectric behaviour of lithium doped zinc fluoride. All issues are brought together in Chapter 7 for further discussion and conclusions and suggestions for areas of further work are given in Chapter 8. Finally, Appendix A details the thermodynamic approximations inherent in the mass action method.