Chapter 8

Summary

This last chapter provides an overall picture of the research presented in this thesis and suggests areas where work remains to be done. In Chapter One we presented examples of the uses of CeO_2 and in particular discuss its application as an SOFC and co-catalyst in car exhaust systems. These uses can be related to the defect and surface chemistry exhibited by CeO_2, in particular, the variable valence exhibited by the cerium ions and the presence of charge compensating oxygen vacancies. A short overview of the literature on CeO_2 was also provided. Chapter Two provides a brief overview of the history of computer simulation and discuss the theoretical basis of computer modelling.

Studies of bulk CeO_2 are presented in Chapter Three. Isolated defect calculations were performed on both stoichiometric and non-stoichiometric ceria doped with Cd and In. The results indicate that when doped with Cd, the resulting oxygen vacancy prefers to occupy a first nearest neighbour site with respect to the impurity. For an In dopant this is not the case; the compensating oxygen vacancy has a equal preference for both the 1st and 2nd neighbour sites. These results are in agreement

with the hyperfine experiments of Gardner and co-workers. For $(2M_{Ce}^{|}\!:\!V_O^{\bullet\bullet})^X$ clusters the lowest energy configuration is that which has at least one of the impurity ions residing at a 2nd site with respect to the oxygen vacancy. This is true for both stoichiometric and non-stoichiometric CeO_2. A similar behaviour is seen in undoped non-stoichiometric ceria where the lowest energy configuration is that where one of the polarons sits at a second site.

In Chapter Four two different defect models were considered in order to study the nature of defect - defect interactions in MgO doped with high concentration of Al_2O_3, a so called 'ideal system'. One of the models assumes the defect clusters are isolated and hence have only a volume effect. The second model considers both inter-cluster and intra-cluster interactions. Both models agree well with the experimental data and indicate trimer defect clusters are the dominant defect species. In the high concentration region the isolated defect model gives a lattice parameter close to the experimental value. The LUC model in this region gives a spread of lattice parameters, whose average is close to the isolated defect model. Given this, the isolated defect model provides a computationally efficient method of estimating the lattice parameter and structures of highly defective materials and will be useful in studying highly defective CeO_2 systems.

Perfect and defective surfaces are studied in the subsequent chapters (Chapter 5 and 6). In the study of perfect surfaces we examine the dependence of the crystal morphology and surface structure on the choice of potential parameters used. The results show that a previously used model is inadequate for modelling high index faces. Additionally, the surface and attachment energies were examined as a function of misorientation angle. An attempt to explain the trend in surface energies is made

by correlating it to the number of bonds broken per unit area when a surface is created.

The chapter on non-stoichiometric surfaces of CeO_2 exams a number of defect configurations on some of the important faces. The relaxed structure of the configuration is dependent on the surface; the (200) face rearranges to allow the vacancy to migrate to the surface. Conversely the (331) adjusts itself such that the vacancy is just below the surface. For the (111) and (220) planes the surface rearranges so as to reduce the defect dipole in the Z-plane. When studying defect formation energies on the surface, a strong correlation is seen between the defect formation energy and the surface area. This indicates that defect-defect interactions are significant on some surface and should be examined in greater detail in future work.

Finally, we use MD to study the behaviour of two CaF_2 nanoclusters. The results obtained in this study may be used as a basis for future studies of CeO_2. After equilibration, for both clusters, the type III faces have a surface structure similar to that required to stabilise dipolar faces in the static surface calculations. This justifies the approach used in previous studies static surface studies. Additionally, studies of melting and solidification were carried out on the smaller crystallite. It was found that Frenkel defects form at $\approx 1000K$; that the fluorine sub-lattice melts over a period of about 10ps and a temperature range of 150K. The calcium lattice on the other hand, melts over a much shorter time scale, 4.5ps. The melting temperature of the cluster is 1750K, which is very close to the experimental value of 1696K.

Attempts were made to re-crystallise the cluster using a range of equilibration times and cooling rates. For the slowest cooling rate, the FT of calcium sub-lattice begins to show some level of ordering. The is a potentially important observation

upon which future work must concentrate. However, in all other cases the clusters form glassy solids.