

# Atomic Scale Disorder in Fluorite and Fluorite Related Oxides

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# Abstract

Atomistic simulation techniques have been used to calculate a variety of disorder properties in oxides with the fluorite structure and the pyrochlore structure (which is fluorite related).

Chapter 1 introduces pertinent concepts such as crystallography, point defect equilibria, surface types and transport theory. Chapter 2 discusses the methodology of bulk, surface, perfect and defective lattice calculations.

Chapter 3 and 4 are concerned with  $\text{UO}_2$ . Chapter 3 presents results of fission product solubility calculations in  $\text{UO}_2$ . In particular, the solution of Kr, here calculated classically, is compared to similar *ab initio* calculations of other researchers. Chapter 4 builds upon these results by discussing the segregation of fission products to the stable, low index (111), (110) and (100) surfaces of  $\text{UO}_2$ . It is shown that the segregation behaviour depends on fission product chemistry, charge, size as well as surface.

In Chapters 5 and 6, aspects of the defect behaviour of pyrochlore oxides are investigated. Chapter 5 discusses mechanisms to generate non-stoichiometry in a broad range of pyrochlore compounds. Calculations are presented in the form of a contour map, in order to convey the large amount of information. These results are compared with experimental phase diagrams. Chapter 6 predicts the existence of heretofore unobserved pyrochlore compounds,  $\text{Dy}_2\text{Hf}_2\text{O}_7$ ,  $\text{Ho}_2\text{Hf}_2\text{O}_7$  and  $\text{Er}_2\text{Hf}_2\text{O}_7$ .

This prediction is made by comparing calculated local order-disorder energies with the corresponding order-disorder temperatures obtained from phase diagrams.

The concluding chapter summarizes the results of this thesis and offers ideas and details for potential future work. Projects involving both bulk and surface simulations are proposed.

Appendix A describes the segregation of  $\text{Y}_2\text{O}_3$  to surfaces of t- $\text{ZrO}_2$ .

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