Atomic Scale Disorder in Fluorite and Fluorite Related Oxides

A dissertation submitted to the University of London
for the degree of Doctor of Philosophy
and the Diploma of Imperial College

by
Christopher R. Stanek

Department of Materials
Imperial College of Science, Technology and Medicine

August 2003

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 UO_2. Chapter 3 presents results of fission product solubility calculations in 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 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, $Dy_2Hf_2O_7$, $Ho_2Hf_2O_7$ and $Er_2Hf_2O_7$.

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 Y_2O_3 to surfaces of t-ZrO_2.

Acknowledgements

In a classic oversight, I arrived in London without a pillow, blanket, utensils, etc., and immediately learned that I would need to rely on a fairly sturdy support network if I was to make it through this process. During the said process, as important as the science I have learned has been the reiteration of the importance of family and friends. It is therefore inappropriate to continue without thanking a few of these people.

It would also be inappropriate not to start by thanking my advisor, Prof. Robin W. Grimes. Exemplifying the ideal advisor from the student perspective (the only one I can speak on), Robin went and continues to go far beyond the call of duty for all of his students, of which I was fortunate enough to have been one.

The Atomistic Simulation Group at Imperial College was a wonderful place to work. Thanks to Michael Abramowski for taking time (a non-negligible amount) in order to show me the ropes, to Kurt Atkinson for not only keeping us up and running, but for being a good friend, to Mark Levy for filling kjwa's void, to Licia Minervini for not only introducing me to the group, but also serving as an advisor of all sorts, and to Mohsin Pirzada for teaching an American a thing or two about cricket.

Many thanks to the friends I made in London, especially: the entire 14 Bramber Rd. contingent (Ben, Donna, Kimiko, *et al.*), for the use of a comfy (if not rather

dingy) chair, for humouring my preference of Tandoori Garden over North End Tandoori and for providing a place I looked forward coming home to; and Brad Carmady for augmenting my collection of near death stories.

Los Alamos National Laboratory was a worthwhile hiatus from London, and the people there made my visit more so enjoyable. I believe this thesis has greatly benefitted from my stay (most of Chapters 5 and 6 were written on the lifts at Pajarito Mt. or at the Tesuque Village Market). However, it would not have been as fruitful if it weren't for the interaction I was able to have with the Los Alamos scientists. I appreciate their openness and willingness to work with a visiting Ph.D. student.

The University of Colorado at Boulder unknowingly provided invaluable library resources. I am not certain who to thank, but feel it in my karmic interests to do so. Also, thanks are in order to my Physics 112 and 211 students, for helping me to learn physics.

Each member of the Henwood family contributed to the completion of this thesis. Their kindness and generosity is without parallel.

The entirety of my family did not let a lack of geographic proximity interfere. For allowing me to explore, I am indebted to you Mom, Kate, Dan and especially my Dad, to whom I dedicate this thesis.

And finally, my utmost gratitude to CH, for believing in the promise of better times.

Copyright

Contents

List of Tables

List of Figures