Crystal Structure and Defect Property Predictions in Ceramic Materials.

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Abstract

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

Initial investigations were made of ABO_3 perovskite materials. Crystal structure predictions were an essential precursor to more in depth studies of the perovskite defect structures. The two cations A and B were restricted to being trivalent, and the anion to be oxygen; in total 96 separate compositions were studied. Structural changes between rhombohedral $R\bar{3}c$, orthorhombic Pnma, hexagonal $P6_3cm$ perovskite and cubic bixbyite Ia3 were correlated to cation radii via a two dimensional contour map.

Calculations of the internal energies for intrinsic defect formation were then undertaken over the extensive ABO_3 compositional range. These results were then compared to previous work on a series of pyrochlore materials. The motivation stemmed from a correlation that had been made between intrinsic defect formation and radiation tolerance in the pyrochlore materials. Using this same idea, the relative radiation tolerance between different ABO_3 compounds is proposed and the relative radiation tolerance compared to pyrochlores is discussed. It was found that

of the compositions under consideration, only the Ia3 bixbyite materials could be as tolerant as the pyrochlore materials.

Maintaining the theme of energy systems, the suitability of a subset of the perovskite oxides was assessed for their application as solid oxide fuel cell components. This required a consideration of the defect behaviour of these materials when aliovalently doped. Thus an investigation into the possible compensation mechanisms operating when a range of divalent cations are substituted into the materials was carried out. The lowest energy solution mechanisms involved charge compensation via oxygen vacancies and the specific solution site was dependent on both the crystal structure of the perovskite and the size of the divalent ion.

The dielectric behaviour of lithium doped zinc fluoride was also investigated. Previously it had been determined experimentally that lithium doping of zinc fluoride results in an anisotropic dielectric relaxation. The mechanism has been unresolved since the early 1970s, however, through atomistic simulations it has been possible to develop a defect model that is able to describe this anisotropy. A new defect model involving a split lithium interstitial defect cluster formation is proposed.

The different solid state issues addressed by this thesis are linked through a central theme which emphasises the importance of atomic scale defect processes in inorganic materials, and their interaction with different crystal structures.

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