Chapter 7

Conclusions

7.1 Crystal Structure Predictions for Perovskites

The results presented in the preceding chapters show a high degree of agreement with experimental work when the situation is limited to where the A and B cation ratio remains stoichiometric, i.e. the perovskite structure is maintained and not permitted to dissociate to form garnet.

When the constituent cation radii are highly disparate, a rhombohedral R$\bar{3}$c structure is adopted; as the radii become more similar, first an orthorhombic Pnma structure results, followed by a hexagonal P6$_3$cm structure. Finally as the cation radii become most similar (for the compounds under consideration) a cubic bixbyite is formed. One of the major driving forces for the change in crystal structure is the change in the oxygen sublattice, as at small distortions, the BO$_6$ octahedra begin to tilt away from their ideal cubic orientations forming rhombohedral and orthorhombic symmetries, and then as the lattice strain increases, the octahedra themselves

are broken, such that for the $P6_3cm$ structure the A and B cation sites are seven and five coordinated respectively.

Structure and defect energies have been predicted for a number of compounds that have not previously been reported. These include a number of compounds within the $AAlO_3$, $ACrO_3$, $AGaO_3$, $AFeO_3$, $AScO_3$ and $AInO_3$ regions.

Changes in the potential model are unable to describe the dissociation of the perovskite to garnets. It is possible that a new potential model is needed, or that subtly different potential sets should be utilised for the garnet and perovskite symmetries (however this in turn would introduce consistency problems).

7.2 Intrinsic Defect Processes in Perovskites: Implications for Radiation Tolerance

The antisite reaction is the dominant intrinsic defect reaction mechanism for the majority of the 3:3 perovskite compounds under consideration. When the constituent cation radii are highly disparate (the $R\bar{3}c$ and the least distorted Pnma structures being dominant) the Schottky reaction is the dominant process. For the $P6_3cm$ compounds, the Schottky reaction energy is higher than the anion Frenkel reaction energy. The cation Frenkel reaction energy is always the highest energy process.

By relating the energies for defect processes to radiation tolerance, predictions of how the radiation tolerance varies across an extensive series of $A^{3+}B^{3+}O_3$ compositions is possible. Disorder on the cation sublattice is a direct effect of irradiation and is a major contributing factor to the retained energy, while disorder on the oxygen

sublattice defines the recovery processes. The combined effect of these processes are therefore necessary to predict the radiation tolerance of the materials. A low energy for the antisite defect process in itself, is insufficient for a radiation tolerant material. Therefore, the combined effect of the defect processes is used to predict the radiation tolerance, which follows the classical perovskite tolerance factor in that tolerance increases $R\bar{3}c < Pnma < P6_3cm < Ia3$.

By comparing the equivalent defects in $A_2B_2O_7$ pyrochlore oxides with previous simulations, the relative tolerance of ABO_3 oxides can be assessed. Significant for the bixbyite forming materials, the oxygen Frenkel energy is similar to the oxygen Frenkel of pyrochlores. For example, on such a basis, none of the perovskites would be expected to exhibit the exceptional radiation tolerance of the zirconate or cerate pyrochlores/fluorites. However, the best perovskites would have a similar tolerance to the intermediate titanate pyrochlores.

Clearly, the low defect formation energies exhibited by the bixbyite oxides are consistent with these materials being approximately as radiation tolerant as the better pyrochlores. It seems logical to assume that this is in part a consequence of the similarity between the bixbyite and fluorite structures [146].

Finally, the equivalence of charge between A^{3+} and B^{3+} cations in the perovskite systems does not aid the tolerance of the perovskites as the difference in ion size and the associated crystallography means that these materials should not be highly radiation tolerant due to the inherent lattice strains introduced upon disorder. Conversely, materials with the bixbyite structure should show considerable tolerance.

7.3   Extrinsic Defect Processes in Perovskites

For the four compositions considered ($GdInO_3$, $GdScO_3$, $LaInO_3$, $LaScO_3$), the lowest energy compensation reaction is the oxygen vacancy mechanism for all divalent solute cation radii. Furthermore, the smallest dopants will substitute on B sites and the largest on A sites. However, the dopant radius at which this change in lattice site preference occurs is a function of both lattice composition and crystallography.

Due to this crystallographic condition for solution, the orthorhombic compound is more sensitive to solution site than the hexagonal materials. This is due to the relative sizes of the A and B lattice sites, which in turn is related to the coordination of those sites. Very small dopants substitute exclusively at the B lattice site in the orthorhombic material, followed by an intermediate stage whereby solution occurs on both lattice cation sites, and finally larger cations substitute only onto the large A site. In the hexagonal materials, most of the dopants substitute onto the B lattice site, with only the largest substituting onto the A lattice site, with no intermediate stage.

A further consequence of this crystallographic variation is that the energy is higher for solution into the orthorhombic $LaScO_3$ than into the three hexagonal compounds ($LaInO_3$, $GdScO_3$ and $GdInO_3$). Therefore, the concentration of oxygen vacancies that would be formed is lower in the $LaScO_3$ than in the other compositions.

7.4   Lithium doped Zinc Fluoride

Solution energy calculations clearly support the case that the dielectric relaxation is governed by lithium interstitial ions. The split lithium interstitial cluster configuration predicted here is, however, quite distinct from models previously put forward. (This is isostructural to the split F^- interstitial ion reported in the intrinsic defect analysis). The cluster consists of two equivalent Li^+ interstitials either side of a vacant zinc site (i.e. $\{Li_i^\bullet : V_{Zn}'' : Li_i^\bullet\}^X$).

The split Li^+ interstitial cluster cannot be responsible for the anisotropic dielectric relaxation due to its symmetry and inability to couple into a field. However, solution energy analysis suggests that the experimental material was far from equilibrium. The supersaturated solid solution consisted of essentially immobile substitutional Li^+ ions and charge compensating Li^+ interstitial ions. These latter defects are confined to move preferentially in [001]. Any untrapped Li^+ interstitial ions will move in [001] subject to an applied field. It is the displacement of these non-equilibrium, residual defects that may conceivably result in a polarization of the crystal. Certainly such a polarization will occur much more strongly in [001] than in the ab plane. Furthermore, the polarization will decay once the temperature is raised to overcome the activation energy barrier. Nevertheless, such defects should eventually become trapped and as such the anisotropic relaxation effects may be subject to a form of thermal cycling fatigue.