

# Chapter 8

## Further Work

### 8.1 Simulation Studies

#### Crystal Structure Predictions

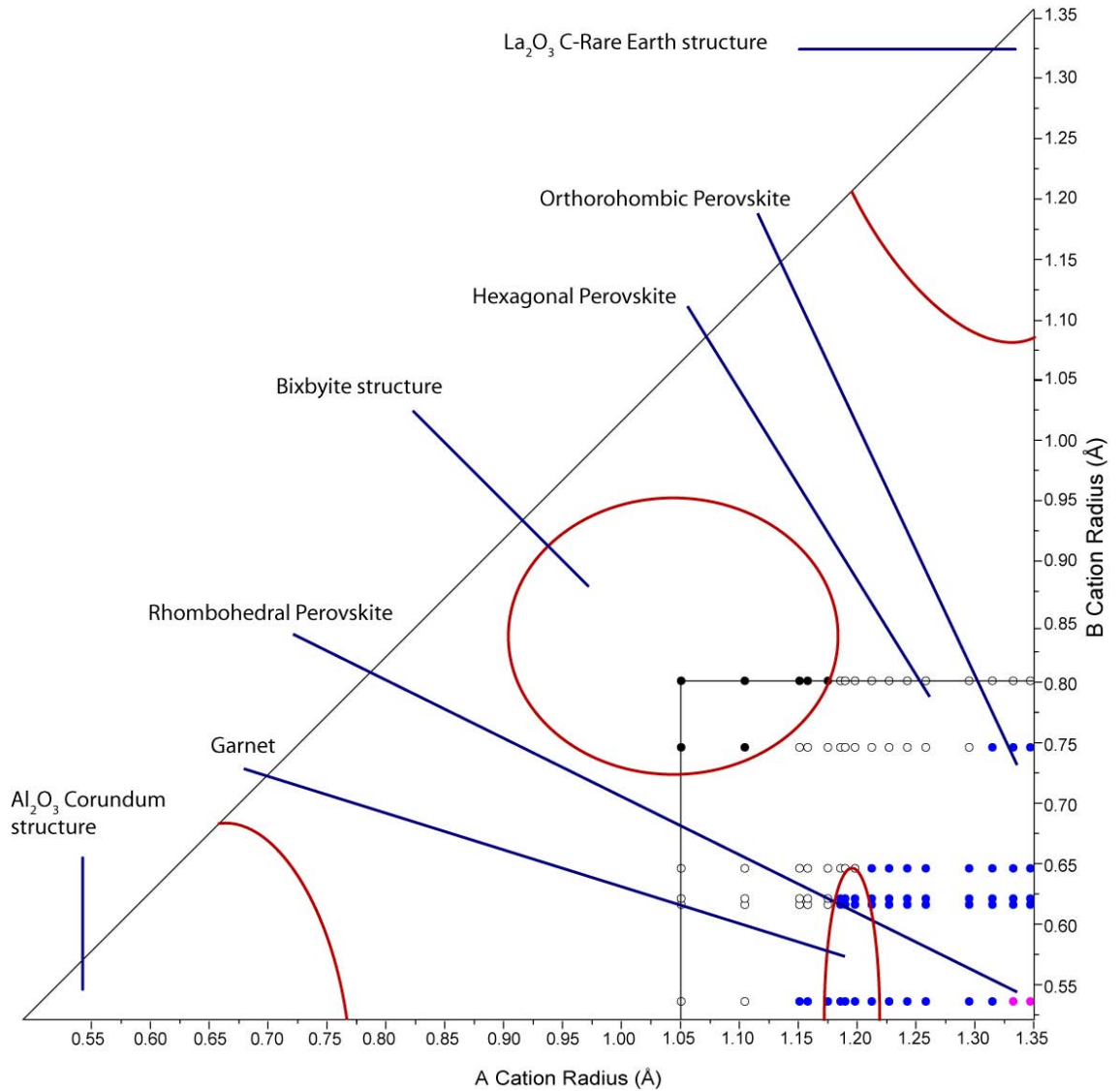
While much has been learnt from the current simulation studies, the crystal structure predictions for the current set of  $A^{3+}B^{3+}O_3$  materials should be revisited so that the dissociation of the perovskite to the two garnets can be further investigated. At present, there are limitations in the potential model such that the same consistent set of potentials are unable to predict both the different perovskite phases and the formation of the garnets. A useful tool to overcome this limitation would be quantum mechanical calculations. Initial results for the perovskite materials have been presented here, however a more in depth study should be able to determine more clearly the structural boundaries for crystal structure changes. This will present a significant challenge due to the size of the unit cells; the smallest cell is the rhombo-

hedral ( $R\bar{3}c$ ) perovskite with 16 ions, the next in size is the orthorhombic (Pnma) perovskite with 32 ions, the largest perovskite is the hexagonal ( $P6_3cm$ ) with 48 ions, whilst the garnets are significantly larger than any of these with the smaller having 96 ions per cell and the largest with 256 ions per cell. The size of the unit cells for the hexagonal perovskite and the two garnet phases means that quantum mechanical simulations on these structures are hugely demanding computationally.

The compositional range investigated with pair potentials should be extended to encompass a larger array of compounds ranging from corundum oxides e.g. ( $Al_2O_3$ ), bixbyite and  $La_2O_3$  structure. A proposed expansion of the ionic radii space is provided in Figure 8.1. This would allow for more significant crystal structure variations to be compared, and in turn aid in the understanding of the inter dependence of crystal structure variation and dominant defect processes. For example, Figure 8.1 shows that the corundum structures are likely to be developed when both the A and B cations are small, outside the scope of the current investigation.

Additionally, new potential parameter sets could be developed to better describe the lattice. Those currently planned are a new breathing shell model in which the radius of the oxygen shell is allowed to alter with respect to the local atomic environment. The breathing shell model is useful as it better describes how the electron density of an ion is deformed as the surrounding atoms squeeze it. It is possible that the breathing shell model may not be sufficiently flexible to describe the wide array of ion environments since this is still a centrosymmetric model. Therefore elliptical distortions to the shell model could also be incorporated, thus allowing the shell to breath and distort.

The free-energy of the system should also be calculated in order to account for the effect of temperature on the lattice. This essentially raises the calculation tem-



**Figure 8.1:** Proposed extension to the crystallographic space modelled.

perature from zero kelvin to better compare with the experimental data which is after all mostly derived from room temperature measurements. Currently the GULP code [88] only calculates the Helmholtz free energy, however, the newer SHELL code [246] is able to calculate the Gibbs free energy. The Helmholtz free energy does not contain the pressure-volume (PV) term that is included in the Gibbs free energy, and is therefore only a measure of the internal energy of the system rather

than the enthalpy of the system.

## Radiation Tolerance

The effect of defect clusters was considered only briefly in the course of this thesis, however, defect association plays a major role in determining materials properties. Therefore, the way in which the intrinsic defects associate within the perovskite materials should be investigated further. Defect clustering is not only of significance to the radiation tolerance of the materials, it also gives information regarding the behaviour of the majority intrinsic defects and will be an important precursor to further studies of these perovskite materials for many potential applications, from dielectric resonators to SOFCs.

During the storage of radioactive waste, one problem that is encountered is that the defects formed lead to lattice swelling. This in turn leads to micro-cracking which provides fast ion migration pathways and thus leaching of the waste ions into the environment. This effect can be modelled by calculating the defect volumes of both the isolated and defect clusters. These volumes can be determined by two different approaches which should be compared. The first is via the construction of a supercell in which the defect concentrations can be altered. The volume of this cell is then determined and compared to the value of an equivalent perfect lattice cell. The second approach calculates the defect volume by comparing defect calculations conducted under constant volume and constant pressure conditions [247].

Defect migration studies could also be used to investigate defect recovery processes that occur in the perovskites post irradiation damage. These could be carried out either using the static lattice method employed in this thesis for the work on the

dielectric relaxation of lithium doped zinc fluoride, or via a molecular dynamics approach.

## Extrinsic Defect Processes

Since the defect of importance for SOFCs is the oxygen vacancy, the clustering of the intrinsic defects is particularly important as this will help develop an understanding of possible trapping mechanisms for the majority charge carriers and a better measure of the defect concentrations.

The doping studies should be expanded to include the substitution of different ions onto both the A and the B lattice sites. This would lead to complex defect association and the interaction energies between defects would then also need to be determined.

The transport of ions through the lattice should be studied with particular attention to the mobility of oxygen anions and oxygen vacancies. It is the conductivity of these species that underpins the SOFC efficiency. This can be achieved using molecular dynamics calculations, however if the timescales that need to be modelled are larger than can normally be handled with standard techniques, accelerated dynamics approaches can be employed [21, 248].

## Dielectric Relaxation of $\text{ZnF}_2$

In order to more fully understand the motion of the lithium defect within zinc fluoride, molecular dynamics calculations should be conducted. Such calculations would

be able to more conclusively determine the possible migration paths of these defects. It would also be useful to conduct supercell calculations in which the concentration of the defects can be altered. A further method can be employed which uses a combination of static lattice energy minimization and Monte Carlo procedures [249]. In this combined approach, the energy minimization process identifies the configuration with the lowest lattice energy (i.e. the perfect lattice structure), the Monte Carlo procedure is then used to sample higher energy states for use with a defined thermodynamic analysis. Energy minimization is applied after each random redistribution of defects to obtain the energy corresponding to each new arrangement. This would further the argument that the lithium defects do indeed cluster in zinc fluoride.

Also, to consider the anisotropic dielectric response of the doped  $\text{ZnF}_2$  more fully, it would be useful to compare similar doping schemes in related tetragonal fluoride materials such as  $\text{MgF}_2$  and  $\text{NiF}_2$ .

## 8.2 Experimental Studies

### Crystal Structure Predictions

The temperature dependant crystal structure of the  $\text{A}^{3+}\text{B}^{3+}\text{O}_3$  compounds should be determined using modern *in situ* X-ray diffraction techniques. Much of the current experimental structural data is inconsistent and dates back to before the 1960s. There are also some regions of the composition field where no data exists to describe ion positions. There are also structural data which would appear erroneous, for example there is evidence that the material is a perovskite, yet investigations

by other authors show that the perovskite phase is unstable at room temperature and that the material should disassociate into two garnet phases. This fundamental research is important because the  $A^{3+}B^{3+}O_3$  materials are used in a variety of industrial applications, and in order to make real advances, it is vital to understand the optimisation of properties (an example of this is given in Chapter 3 for the discussion of the dielectric properties).

Data on the evolution of the structures as a function of temperature would enable the illustration of the interconnections between the different crystallographies. This is also important as many of the applications of these perovskite compounds require their operation at elevated temperatures. This work should also look at the structural evolution to very low temperatures so that more consummate comparison can be made with the calculated predictions.

## **Radiation Tolerance**

Further experimental work will be needed to test the prediction that the perovskites are less radiation tolerant than all the fluorite related materials. It would also be interesting to carry out a series of experiments as a function of ion irradiation fluence to see if it is possible to differentiate between the various perovskites and relate this to the predictions made herein.

## **Extrinsic Defect processes**

The next step in determining the suitability of the perovskite compounds for SOFC applications is to measure the oxygen conduction across specimens, both pure and

doped. This would allow for accurate operating temperatures to be calculated and the relative suitability of different materials to be assessed. Some of the current problems being encountered when using certain compositions is that they dissociate partially and form second phases at the grain boundaries. These phases are of the garnet type. Therefore if these phases are formed explicitly there should be no second phase formation, and the compositions can be tested for their conductivity properties.

## Dielectric Relaxation of $\text{ZnF}_2$

Current experimental results suggest a significant anisotropy in the dielectric response to an electric field. The simulation studies suggest that this dielectric anisotropy is due to non-equilibrium defects. Such defects should eventually become trapped and as such the anisotropic relaxation effects may be subject to a form of thermal cycling fatigue. An experiment based on this premise may provide one way of further investigating this material. Alternatively, samples could be subjected to higher temperature heat treatments so that they are closer to obtaining an equilibrium defect configuration. In this latter case, a significant anisotropic response would not be expected. In order to compare the response of the  $\text{ZnF}_2$  lattice to the electric field, it would be useful to compare equivalent experiments to other tetragonal fluoride materials such as  $\text{MgF}_2$  and  $\text{NiF}_2$ .