Chapter 3

Perovskite Perfect Lattice

3.1 Perovskite Compositions

The mineral perovskite (CaTiO₃) is named after a Russian mineralogist, Count Lev Aleksevich von Perovski, and was discovered and named by Gustav Rose in 1839 from samples found in the Ural Mountains [95]. Since then considerable attention has been paid to the perovskite family of compositions. The perovskite is a true engineering ceramic material with a plethora of applications spanning energy production (SOFC technology) [96], environmental containment (radioactive waste encapsulation) [97] and communications (dielectric resonator materials) [98]. Of the more exotic applications, LaGaO₃, PrGaO₃ and NdGaO₃ are being considered as substrates for epitaxy of high T_c superconductors [99].

3.2 Crystallography of The Perovskite Structure

The perovskite structure has the general stoichiometry ABX_3 , where "A" and "B" are cations and "X" is an anion. The "A" and "B" cations can have a variety of charges and in the original Perovskite mineral (CaTiO₃) the A cation is divalent and the B cation is tetravalent. However, for the purpose of this study, the case where both the A and B cations adopt a trivalent state were considered and the A cations were restricted to being rare earths. Due to the large number of perovskite compositions possible from combinations of cations on the lattice site, 96 compositions were chosen. The ions occupying the A and B lattice sites are detailed in Figure 3.1.



Figure 3.1: Schematic of compositions under study.

The traditional view of the perovskite lattice is that it consists of small B cations within oxygen octahedra, and larger A cations which are XII fold coordinated by oxygen. This structural family is named after the mineral CaTiO₃ which exhibits an orthorhombic structure with space group Pnma [100, 101]. For the $A^{3+}B^{3+}O_3$ perovskites the most symmetric structure observed is rhombohedral R3c (e.g. LaAlO₃) which involves a rotation of the BO₆ octahedra with respect to the cubic structure. However, this distortion from the perfect cubic symmetry is slight [100].

The structure of an ideal cubic perovskite is shown in Figure 3.2, where the A cations

are shown at the corners of the cube, and the B cation in the centre with oxygen ions in the face-centred positions. The spacegroup for cubic perovskites is $Pm\overline{3}m$ (221) [102]; the equivalent positions of the atoms are detailed in Table 3.1.



Figure 3.2: Cubic perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen anions forming an octahedra.

Site	Location	Co-ordinates
A cation	(2a)	(0,0,0)
B cation	(2a)	$\left(rac{1}{2},\ rac{1}{2},\ rac{1}{2} ight)$
O anion	(6b)	$\left(\frac{1}{2}, \frac{1}{2}, 0\right) \left(\frac{1}{2}, 0, \frac{1}{2}\right) \left(0, \frac{1}{2}, \frac{1}{2}\right)$

Table 3.1: Atomistic positions in cubic perovskites [103]

The rare earth perovskites have been widely studied using X-ray diffraction and neutron scattering techniques (see Section 3.3). The first study was carried out in 1927 by Goldshmidt [104] which concentrated on YAlO₃ and LaFeO₃ [105]. Many early studies reported that the perovskites showed mainly cubic or pseudocubic structure, but as work on these systems continued, the number of proposed symmetries increased. The lack of conclusive structural determinations amongst these early studies are likely due to the relative inaccuracies of the X-ray photographic techniques and are compounded by the small magnitude of the structural distortions [105]. Recent studies have been able to more accurately determine the structure of some perovskites that can then be used as a foundation for subsequent modelling. Literature suggests that many of the materials exhibit the orthorhombic Pnma [106] (or Pbnm) [99, 107] distorted structure at room temperature. This distorted structure can be seen in Figure 3.3 (it is double the size of the cubic cell). Special positions for the Pnma distortion are given in Table 3.2. A further distortion is also possible resulting in a rhombohedral structure with the space group R3c [102, 108, 109]. The rhombohedral structure is shown in Figure 3.4; special positions are given in Table 3.3. A further distortion can be seen with the formation of an hexagonal $P6_3$ cm structure, which can be seen in Figure 3.5, with special positions given in Table 3.4. In this variant, the lattice distortions are so great that the A cations are now VII coordinate and the B cations are V coordinate and the structure has lost its direct similarity with the perovskite symmetry. As such, although these are sometimes referred to as perovskites, they are not strictly perovskite structures and are best considered as intermediate between the perovskite and bixbyite or garnet structures.

Beyond the hexagonal region, a cubic bixbyite (space group Ia3) [110] structure is formed illustrated in Figure 3.6, details are given in Table 3.5. For this structure, the cation sites are equivalently octahedrally coordinated by oxygen, and as such the difference between the A and B lattice sites are negligible.

One description of the perfect perovskite structure is to consider corner linked BO_6 octahedra with interstitial A cations as discussed by Hines *et al.* [112]. In an idealised cubic perovskite constructed of rigid spheres, each cation is the perfect size to be in contact with an oxygen anion; the radii of the ions can then be related:



Figure 3.3: Pnma, orthorhombic perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, with red spheres representing oxygen ions.

Ľa	ble	3.2	2:	Atomist	ic position	ns in	orthorho	mbic per	ovskites	[103].	

Site	Location	Co-ordinates
A cation	(4c)	$\pm [(\mathrm{u},\mathrm{v},rac{1}{4})(rac{1}{2}\text{-}\mathrm{u},\mathrm{v}{+}rac{1}{2},rac{1}{4})]$
B cation	(4b)	$(\frac{1}{2}, 0, 0) \ (\frac{1}{2}, \frac{1}{2}, 0) \ (0, 0, \frac{1}{2}) \ (0, \frac{1}{2}, \frac{1}{2})$
O(1) anion	(4c)	$\pm [(m, n, \frac{1}{4}) (\frac{1}{2}-m, n+\frac{1}{2}, \frac{1}{4})]$
O(2) anion	(8d)	$\pm[(x, y, z) (\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z) (-x, -y, z+\frac{1}{2})$
		$(x+\frac{1}{2}, \frac{1}{2}-y, -z)]$

u, v, m, n are dependent on the particular structure under consideration.

$$R_A + R_O = \sqrt{2(R_B + R_O)}$$
(3.1)

where, R_A , R_B , and R_O are the relative ionic radii of the A site and B site cations and the oxygen ion respectively.



Figure 3.4: $R\overline{3}c$ rhombohedral perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen.

Site	Location	Co-ordinates
A cation	(6a)	$(0, 0, \frac{1}{4})$
B cation	(6b)	(0, 0, 0)
O anion	(18e)	$(x, 0, \frac{1}{4})$

Table 3.3: Atomic positions for rhombohedral perovskites [102].

n.b. the above co-ordinates are based on hexagonal axes.

However, with decreasing A cation size, a point will be reached where the cations will be too small to remain in contact with the anions in the cubic structure. Therefore the B-O-B links bend slightly, tilting the BO₆ octahedra to bring some anions into contact with the A cations [112]. To allow for this distortion, a constant, t, is introduced into the above equation, thus:

$$R_A + R_O = t\sqrt{2}(R_B + R_O) \tag{3.2}$$



Figure 3.5: $P6_3$ cm hexagonal perovskite unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen.

Site	Location	Co-ordinates
A cation	2a	(0, 0, z)
A cation	4b	$\left(\frac{1}{3},\ \frac{2}{3},\ \mathrm{z}\right)$
B cation	6c	(x, 0, z)
O(1) anion	6c	(x, 0, z)
O(2) anion	6c	(x, 0, z)
O(3) anion	2a	(0, 0, z)
O(4) anion	4b	$(\frac{1}{3}, \frac{2}{3}, z)$

 Table 3.4: Atomic positions for hexagonal perovskites [111].

The constant, t, is known as the tolerance factor and can be used as a measure of the degree of distortion of a perovskite from ideal cubic. Therefore, the closer to cubic, the closer the value of the tolerance factor is to unity [113]. This distortion



Figure 3.6: Bixbyite unit cell. Blue spheres represent the cations, and red spheres represent oxygen. The A and B cations are distributed over all of the cation sites.

Site	Location	Co-ordinates
A/B cation	8b	$\left(\frac{1}{4},\ \frac{1}{4},\ \frac{1}{4}\right)$
A/B cation	24d	$(x, 0, \frac{1}{4})$
O anion	48e	(x, y, z)

 Table 3.5: Atomic positions for cubic bixbyite [110]

from cubic to orthorhombic is shown in Figure 3.7. All perovskite distortions that maintain the A and B site oxygen coordinations involve the tilting of the BO_6 octahedra and an associated displacement of the A cation. For the orthorhombic structure, these octahedra tilt about the b and c axes, while in the rhombohedral structure the octahedra tilt about each axis [99]. This octahedral tilting is related to the sizes of the A and B cations (as described by the tolerance factor), for example AGaO₃ is more distorted than AAlO₃ [99].



Figure 3.7: Perovskite distortion from (a) cubic to (b) orthorhombic.

On the basis of tolerance factor values, it has been proposed [114] that compositions with 1.00 < t < 1.13 will exhibit hexagonal symmetry. It is therefore not surprising that LaAlO₃ adopts the highly symmetric R3c structure since its tolerance factor is 1.02, based on the appropriate VI and XII coordinate radii of Shannon [30]. As the A cation radius decreases and/or B cation radius increases, the tolerance factor decreases. In the perovskite family, this is associated with the octahedra tilting to yield lower symmetry arrangements which, here, gives rise to an orthorhombic structure with space group Pnma. This is only in broad agreement with the predictions provided by the tolerance factor where compositions with t < 1.00 are associated with cubic and orthorhombic symmetry [114]. Even greater deviations lead to a structure with hexagonal P6₃cm crystallography [108].

Limiting values for the tolerance factor have been determined through experiment. For example, Hines *et al.* suggested (solely by analysis of the tolerance factor) that the perovskite will be cubic if 0.9 < t < 1.0, and orthorhombic if 0.75 < t < 0.9 [112]. If the value of t drops below 0.75 the compound has been seen to adopt an hexagonal ilmenite structure (FeTiO₃) [112]. Such an analysis works better for 2+, 4+ perovskites (for which the tolerance factor was originally determined) than for the 3+, 3+ perovskites which were considered here.

3.3 Crystal Structure Predictions

Initial crystallographic data were collected from published literature. Tables 3.6, 3.7 and 3.8 show these data and the corresponding references for the experimentally determined crystal structures for perovskite compositions. A particularly important resource utilised is the Inorganic Crystal Structure Database which is part of the Chemical Data Service at Darebury [29].

Compound	Space Group	Lattice Parameter (a) Å	Reference
CeCrO ₃	$Pm\overline{3}m$	3.89	[115]
$CeFeO_3$	-	3.9	[103]
$CeGaO_3$	-	3.879	[103, 116]
GdMnO_3	-	3.82	[103]
$PrCoO_3$	$Pm\overline{3}m$	3.78	[115]
$PrMnO_3$	-	3.82	[103]
$\rm SmCoO_3$	$Pm\overline{3}m$	3.75	[115]
$\rm SmCrO_3$	$Pm\overline{3}m$	3.86	[115]
SmVO_3	-	3.89	[115]

Table 3.6: Experimentally determined cubic perovskites.

C 1		Lattice	e Parame	eters Å	D
Compound	Space Group	a	b	с	Reference
$CeAlO_3$	P4/mmm	3.7669	3.7669	3.7967	[117]
$CeVO_3$	Pbnm	5.514	5.557	7.808	[118]
CrBiO_3	Tetragonal	7.77	-	8.08	[103]
$DyAlO_3$	Pbnm	5.21	5.31	7.4	[108]
DyFeO_3	Pbnm	5.302	5.598	7.623	[119]
DyMnO_3	Pnma	5.842	7.378	5.28	[120]
ErFeO_3	Pbnm	5.263	5.582	7.591	[119]
$EuAlO_3$	Pbnm	5.271	5.292	7.458	[121]
EuFeO_3	Pbnm	5.372	5.606	7.685	[119]
GdAlO_3	Pbnm	5.247	5.304	7.447	[108]
GdCoO_3	-	3.732	3.807	3.676	[116]
GdCrO_3	Pbnm	5.312	5.515	$7.6\ 15$	[103, 122]
GdFeO_3	Pbnm	5.349	5.611	7.669	[119]
GdScO_3	Pnma	5.742	7.926	5.482	[123]
$HoFeO_3$	Pbnm	5.278	5.591	7.602	[119]
$LaCrO_3$	Pnma	5.479	7.7562	5.5161	[124]
$LaFeO_3$	Pnma	5.5647	7.8551	5.556	[125]
$LaGaO_3$	Pbnm	5.5245	5.4922	7.774	[126]
$LaMnO_3$	Pbnm	5.5367	5.7473	7.6929	[127]
$LaRhO_3$	Pbnm	5.524	5.679	7.9	[128]
$LaScO_3$	Pbnm	-	-	-	[103]
$LaTiO_3$	Pbnm	5.6301	5.5844	7.901	[129]
$LaVO_3$	Pnma	5.5518	7.848	5.554	[130]
$LuFeO_3$	Pbnm	5.213	5.547	7.565	[119]
$NdCoO_3$	Pnma	5.3312	7.5482	5.3461	[131]
$NdCrO_3$	Pnma	5.4798	7.6918	5.4221	[132]
NdFeO_3	Pnma	5.587	7.761	5.4505	[133]
$NdGaO_3$	Pbnm	5.4276	5.4979	7.7078	[107]
$\rm NdMnO_3$	Pnma	5.7119	7.589	5.4119	[106]
NdScO_3	Pbnm	5.555	5.744	7.972	[134]

 Table 3.7: Experimentally determined orthorhombic perovskites.

C I I	C C	Lattice	e Parame	eters Å	D
Compound	Space Group	a	b	с	Reference
NdVO ₃	Pbnm	5.461	5.58	7.762	[118]
$PrCrO_3$	Pbnm	5.444	5.484	7.71	[113]
$\Pr{FeO_3}$	Pbnm	5.482	5.578	7.786	[119]
$PrGaO_3$	Pbnm	5.4526	5.4947	7.121	[99]
$PrMnO_3$	Pbnm	5.450	5.786	7.589	[135]
$PrVO_3$	-	5.48	5.59	7.76	[113]
$PuCrO_3$	-	5.46	5.51	7.76	[113]
PuMnO_3	Pbnm	5.4	5.786	7.589	[135]
$PuVO_3$	Pbnm	5.48	5.61	7.78	[113]
$ScAlO_3$	Pbnm	4.937	5.2321	7.2045	[136, 137]
$\rm SmAlO_3$	Pbnm	5.2912	5.2904	7.474	[119]
$\rm SmFeO_3$	Pbnm	5.4	5.597	7.711	[119]
SmVO_3	-	5.4	5.591	7.68	[138]
TbFeO_3	Pbnm	5.3268	5.5978	7.6406	[139]
YAlO ₃	Pbnm	5.1377	5.2736	7.3085	[140]
$YbFeO_3$	Pbnm	5.233	5.557	7.57	[119]
$YCrO_3$	Pbnm	5.247	5.518	7.54	[141]
$YFeO_3$	Pbnm	5.2819	5.5957	7.6046	[142]
$YScO_3$	Pbnm	5.431	5.712	7.894	[103]

Table 3.7: continued...

In order to elucidate trends, all compositions must be compared in a single figure. This was achieved by ordering the A cations by size (assuming the XII coordinate radii values throughout) along an x-axis and the B cations (using the VI coordinate values) along a y-axis, thereby forming a 2D grid of compounds. Such a plot (contour map) is shown in Figure 3.8 for all 96 compounds for which calculations were performed. (Of course, for the P6₃cm and Ia3 structures, the cations are not XII and VI coordinations, but these values are maintained in order to facilitate comparisons. The radii are therefore simply an order parameter.)

-	۲ ۲	Lattic	e Param	eters Å		Angles		J F
Compound	Space Group	a	q	c	α	β	7	Keterence
$BiFeO_3$	R3CH	5.5775	5.5775	13.8616	90	90	120	[143]
$CeFeO_3$	ı	3.9	I	ı	06	06	06	[103]
$CrBiO_3$	I	7.77	I	8.08	00	00	00	[103]
$GdAlO_3$	ı	10.56	10.56	12.89	06	90.6	06	[108]
$GdCrO_3$	ı	I	I	I	I	I	I	[144]
$LaAlO_3$	$R\overline{3}c$	5.3647	I	13.1114	60.1	06	06	[102]
$LaCoO_3$	$R\overline{3}CR$	5.3416	5.3416	5.3416	60.99	60.99	60.99	[145]
$LaNiO_3$	$R\overline{3}CH$	5.4573	5.4573	13.1601	06	00	120	[125]
$NdAlO_3$	$ m R\overline{3}c$	5.3223	5.3223	12.9292	00	00	120	[102]
$PrAlO_3$	$ m R\overline{3}c$	5.3337	5.3337	12.9766	00	00	120	[113, 121]
$PuAlO_3$	ı	5.33	I	ı	56.07	00	00	[113]

 Table 3.8: Experimentally determined rhombohedral perovskites.

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Figure 3.8: Lattice Energy Contour Map.

The lattice energy for each compound was calculated according to Equation 2.3, assuming each of 17 possible crystal structures reported in the literature for materials with the ABO₃ stoichiometry (including the four mentioned above). From these data the lowest lattice energy was identified for each compound so that an energy value was assigned to each composition. Each composition is also identified in Figure 3.8 by a symbol which indicates its lowest energy structure. Lattice energy contours were then generated (see Chapter 2 for details). Such maps facilitate comparisons and allow identification of compositional ranges that are of particular significance. In this case it was at once clear that the compounds fall into four groups: rhombohedral

 $R\overline{3}c$, orthorhombic Pnma, hexagonal P6₃cm, and bixbyite Ia3. In this regard it is important to note that although 17 different crystal structures have been reported for ABO₃ compounds in general, some have only been reported for A²⁺B⁴⁺O₃ materials and others represent only slight distortions from those already mentioned.

By studying Figure 3.8 it is apparent that for the situation when the A cation is large and the B cation is small (e.g. LaAlO₃) the lowest energy structure is the rhombohedral R $\overline{3}$ c. As the A cation radius decreases and the B cation radius increases, the lowest energy structure changes to be orthorhombic Pnma. Further decreases in A cation radius and increases in B cation radius result in the formation of the hexagonal P6₃cm structure in which the perovskite structure can only be inferred rather than seen directly. Beyond this hexagonal regime, all resemblance of the perovskite structure is lost and a cubic bixbyite is formed with Ia3 symmetry. Now the A and B cation radii are very similar, and in bixbyite both cation sites are VI coordinated by oxygen. Although dissimilar to perovskite, it is possible to consider bixbyite in terms of a defective fluorite structure [146] (the importance of this is discussed in relation to the radiation tolerance of these phases in Chapter 4).

It is also important to note that despite the abrupt crystallographic changes that are predicted (rhombohedral to orthorhombic to hexagonal to bixbyite) the lattice energy contours are continuous across the boundaries. Thus the lattice or internal energy does not change significantly with the changes in the crystallographic structure.

The prediction of structural types is in overall agreement with experimental data and are consistent with changes in the tolerance factor (see Figure 3.9). The tolerance factor decreases from the point where the rhombohedral structure is dominant (high A cation radius and low B cation radius) to where the bixbyite structure is the lowest energy phase (low A cation radius and high B cation radius). This is consistent with the phase rules derived by Hines *et al.* [112].



Figure 3.9: Classical Tolerance Factor variations as a function of cation radii.

Figure 3.10 shows a comparison between the lowest lattice energy structure predictions to those determined experimentally and presented in Tables 3.6, 3.7 and 3.8. In particular, where an orthorhombic structure is predicted, experimental structures are known to be orthorhombic in most cases. The same holds true for the hexagonal and rhombohedral structures. However, within the orthorhombic and hexagonal regimes, certain compounds are reported experimentally to exhibit slight variations from Pnma and P6₃cm respectively. A similar high degree of correlation is seen for







Figure 3.11: Comparison between experimentally determined and predicted unit cell volumes.

the bixbyite structure. Furthermore, a few compositions in the centre of the map, such as $YFeO_3$, do not form an ABO_3 material, but disproportionate into garnet structures (see Section 3.4).

The degree of agreement between the experimentally determined crystallography and that predicted is further seen by analysing Figure 3.11. This shows that the unit cell volumes of the predicted and experimental structures coincide to a high degree. This figure also shows the crystal structures that have been predicted but not seen experimentally also fit to trends that follow the known experimental data.

3.4 Dissociation to Garnet

Up to this point the assumption has been made that all of the compositions under consideration form as stoichiometric perovskites with a 1:1 ratio of A to B cations. This is not always the case and a number of the compositions dissociate to form garnet compositions. Two garnet compositions are stable; these are $A_3B_5O_{12}$ (spacegroup Ia $\overline{3}$ d) and $A_4B_2O_9$ (spacegroup $P2_1/c$). Thus the decomposition reaction follows:

$$7ABO_3 \rightleftharpoons A_4B_2O_9 + A_3B_5O_{12} \tag{3.3}$$

The crystallography of cubic garnet, $A_3B_5O_{12}$, is shown in Figure 3.12 (with special positions in Table 3.9). This can be thought of as a distorted cubic close packed array of oxygen with isometric symmetry, with BO₆ octahedra and BO₄ tetrahedra forming a framework by alternately sharing corners. The A site forms an AO₈ dodecahedron [147]. The monoclinic garnet variant, $A_4B_2O_9$ is shown in Figure 3.13 (with special positions in Table 3.10). This form is isostructural with the mineral cuspidine (Ca₄Si₂O₇F₂) with the A ion being coordinated by 6 or 7 oxygen ions, and the BO₄ tetrahedra forming B₂O₇ groups by sharing an apical oxygen [148, 149] (in this regard it has some features in common with the ABO₃ P6₃cm varient).

Table 3.9: Atomic positions for cubic (Ia3d) garnet [150].

Site	Location	Co-ordinates
A cation	24c	$(\frac{1}{8}, 0, \frac{1}{4})$
B(1) cation	16a	(0, 0, 0)
B(2) cation	24d	$(\frac{3}{8}, 0, \frac{1}{4})$
O anion	96h	(x, y, z)



Figure 3.12: Garnet (IA $\overline{3}$ D) unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen.



Figure 3.13: Garnet $(P2_1/c)$ unit cell. Blue spheres represent the A cations, yellow spheres represent the B cations, and red spheres represent oxygen.

Site	Location	Co-ordinates
A(1-4) cations	4e	(x, y, z)
B(1-2) cations	4e	(x, y, z)
O(1-9) anions	4e	(x, y, z)

Table 3.10: Atomic positions for monoclinic $(P2_1/c)$ garnet [150].

Figure 3.14 shows a series of phase diagrams for the $Al_2O_3 - RE_2O_3$ system (where RE = rare earth). On these and the following phase diagrams, 2:1 refers to the formation of the monoclinic garnet, $A_4B_2O_9$, and 3:5 refers to the formation of cubic garnet, $A_3B_5O_{12}$. This clearly shows that the structure of the compositions is not straightforward. It can be seen that at equilibrium Dy_2O_3 , Ho_2O_3 , Y_2O_3 , Er_2O_3 , Tm_2O_3 and Yb_2O_3 do not form perovskites when reacted with Al_2O_3 but rather dissociate to form the two garnet phases. Lu_2O_3 also does not form perovskite but instead forms only the cubic garnet. More recent work by Yoshikawa *et al.* [151] has found that several eutectic reactions can be found in this system. La_2O_3 , Ce_2O_3 , Pr_2O_3 , Nd_2O_3 and Pm_2O_3 do not form eutectics with Al_2O_3 ; Sm_2O_3 , Eu_2O_3 , $and Gd_2O_3$ do form eutectics of the form $Al_2O_3/REAIO_3$; Tb_2O_3 , Dy_2O_3 , Ho_2O_3 , Er_2O_3 , Tm_2O_3 , Yb_2O_3 , Lu_2O_3 and Y_2O_3 also form eutectics, however of the form $Al_2O_3/RE_3Al_5O_{12}$ [151].

Figure 3.15 shows a series of phase diagrams for the Cr_2O_3 - RE_2O_3 system. It can be seen that these compounds do form stoichiometric perovskite and no garnet phase has been observed.

Figure 3.16 shows a series of phase diagrams for the Ga_2O_3 - RE_2O_3 system. It is evident that almost all of the rare earth gallate compounds do not form perovskite and indeed only La_2O_3 and Nd_2O_3 form perovskite with Ga_2O_3 . However, both of these also form garnet, La_2O_3 - Ga_2O_3 only forms the monoclinic form, while



Figure 3.14: Phase diagrams for the Al_2O_3 - RE_2O_3 system [152]. Structure types: A, A type rare earth oxide; B, B type rare earth oxide; C, C type rare earth oxide; G, garnet; 1:11, beta alumina; P, perovskite; R, unknown rhombohedral symmetry; α , corundum.



Figure 3.15: Phase diagrams for the Cr_2O_3 - RE_2O_3 system [153]. Structure types: A, A type rare earth oxide; B, B type rare earth oxide; C, C type rare earth oxide; P, perovskite; α , corundum; U, unknown, similar to kappa alumina.

 $Nd_2O_3 - Ga_2O_3$ forms both monoclinic and cubic garnets. Sm_2O_3 and Eu_2O_3 also form both garnet structures (without perovskite formation), and the remaining rare earth sesquioxides form only the cubic garnet with gallia.

Figure 3.17 shows a series of phase diagrams for the $Fe_2O_3 - RE_2O_3$ system. Here, only Nd₂O₃ forms perovskite alone with Fe_2O_3 . All other rare earth sesquioxides form both perovskite and cubic garnet with Fe_2O_3 .

Figure 3.18 shows a series of phase diagrams for the Sc_2O_3 - RE_2O_3 system. Here the situation is changed from the previous diagrams, in that the Sc_2O_3 does not form garnet with the rare earth sesquioxides. La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 and Dy_2O_3 form stoichiometric perovskite, with all remaining rare earth sesquioxide scandia compositions forming solid solutions of the C rare earth type structure.

Similarly in Figure 3.19 shows a series of phase diagrams for the $In_2O_3 - RE_2O_3$ system. Here the rare earth sesquioxides for La - Dy form perovskite, with all remaining rare earth formulations creating solid solutions of the C rare earth type structure.

The information regarding which compositions dissociate to form the garnets and those which remain perovskite is summarised in Figure 3.20.

Further to this, some of the garnet compositions have been manufactured experimentally, however only when high temperatures and pressures were applied [158]. Marezio *et al.* considered the formation of Al, Fe and Ga garnets, and found that at high temperatures and pressure even Y-Fe and Y-Al garnet could be forced to dissociate into perovskite and sesquioxide [158].

It has also proved difficult experimentally to make single phased material in the



Figure 3.16: Phase diagrams for the Ga_2O_3 - RE_2O_3 system [154]. Structure types: A, A type rare earth oxide; B, B type rare earth oxide; C, C type rare earth oxide; P, perovskite; G, garnet; S, spinel; β , beta gallia; K, kappa alumina; U, unknown, similar to kappa alumina.



Figure 3.17: Phase diagrams for the $Fe_2O_3 - RE_2O_3$ system [155]. Structure types: A, A type rare earth oxide; B, B type rare earth oxide; C, C type rare earth oxide; G, garnet; P, perovskite; S, spinel; α , corundum.



Figure 3.18: Phase diagrams for the Sc₂O₃ - RE₂O₃ system [156]. Structure types: A, A type rare earth oxide; B, B type rare earth oxide; C, C type rare earth oxide; P, perovskite.



Figure 3.19: Phase diagrams for the $In_2O_3 - RE_2O_3$ system [157]. Structure types: A, A type rare earth oxide; B, B type rare earth oxide; C, C type rare earth oxide; P, perovskite.



Figure 3.20: Summary of the compositions which form garnets.

region where the garnet is stable. Guo *et al.* [159] states that in attempting to form phase pure YAlO₃ (perovskite YAP) the garnet phase $Y_3Al_5O_{12}$ (YAG) forms as a second phase, and even when attempting to make phase pure YAG, the monoclinic garnet ($Y_4Al_2O_9$, YAM) composition forms as a second phase (along with very small amounts of YAP). Others have found even more phases when attempting to make YAG. In particular, Sim *et al.* used precipitation of hydroxides to try to form phase pure YAG, however they found that at elevated temperature some routes formed an intermediate hexagonal perovskite (rather than the expected orthorhombic) which then transformed into YAG and YAM [160, 161].

Despite this, formation of the perovskite phase is possible if considerable effort is expended. Guo *et al.* [159, 162] use a high energy ball milling procedure borrowed from metallurgy to transform a non-equilibrium Y-Al-O formulation into either YAP or YAG.

In summary, a very sensitive equilibrium exists between perovskite and garnet

phases. Consequently the processing route can induce the transformation between different phases, whilst it remains difficult to manufacture a phase pure sample of any of the phases, garnet or perovskite.

3.5 Discontinuity in the Dielectric Constant

Despite the fact that the dissociation reaction between the perovskite and two garnet phases has been known for some time, this knowledge has not yet started to influence the manufacture of electroceramics. In particular, this means comparison of predicted and experimental dielectric constants is not simple.

Experimental dielectric data is sparse for the $A^{3+}B^{3+}O_3$ compounds, however, a smooth change in the dielectric constant of a series of rare earth aluminate perovskites is suggested [163] (the results have been reproduced in Figure 3.21 for reference). This data clearly shows a gradual increase in the dielectric constant as a function of A cation radius. Such a trend might be expected if it is assumed that the crystal structure is not varying significantly from one composition to the next. The increase is then due to the increase in the polarisability of the A^{3+} cation corresponding to the increase in radius. However, if the inherent assumption that the crystal structure of the compound is constant is not valid then the situation becomes potentially much more complex. Indeed, in the phase diagrams (Figure 3.14) some of these compositions dissociate during formation into the two garnet phases.

The simulation predictions of the static dielectric constant (ϵ_r^0) are shown in Figure 3.22 and the predictions for the high frequency dielectric constant (ϵ_r^∞) are shown in Figure 3.23. In this regard it is important to bear in mind that the interionic



Figure 3.21: Experimentally determined high frequency dielectric constant for rare earth aluminate perovskites [163].

potential model was developed only to reproduce the perfect lattice structures and not other properties. The ϵ_r^{∞} displays some evidence of the crystal structure variation, since as the stability of the orthorhombic perovskite decreases, so does ϵ_r^{∞} . However, if these results for the alumniate compounds are compared to the trend in the experimental dielectric data (Figure 3.21), there is a clear discrepancy. The predicted ϵ_{∞} initially increases to a point where it is at the highest value for all of the perovskites, but then decreases back to a lower value. The predictions are based on the assumption that the perovskite is formed, whereas the experimental data contains possible problems since no structure verification was conducted. A similar trend can be seen for ϵ_r^0 , where the highest values can be found for intermediate A cation radii aluminate materials. All other compounds have a lower value.

In addition to the difference in the trends between the experimental and predicted values of the dielectric constant, the absolute values are also clearly different. The



Figure 3.22: Static dielectric constant predictions for the $A^{3+}B^{3+}O_3$ compounds.

predicted values for the aluminates are too low, with ϵ_r^0 ranging from a 12 to 6. This effect could be improved with the derivation of alternative potential parameter sets, and by using a shell model for the cations. This will be discussed further in the next section.

3.6 Potential Fitting Improvements

Several approaches were used in order to improve the crystal structure predictions both to account for small inaccuracies in the lowest energy perovskite lattice predictions, to include predictions for the formation of the garnet phase and to improve the predicted dielectric constants. The important consideration was that the potentials were altered in a manner so that they maintained their internal self consistency. Full details of the methods attempted are presented in Section 2.3.6.



Figure 3.23: High frequency dielectric constant predictions for the $A^{3+}B^{3+}O_3$ compounds.

The first approach taken was to change the $C_{6,ij}$ parameter such that it was a function of the coordination of the cation for which it was describing. Unfortunately, the alteration of the potentials by making the $C_{6,ij}$ dependent on the coordination of the cation did not affect the structure predictions, and did not improve the agreement with experiment, also only very slight changes in the dielectric properties were seen.

Another change was the inclusion of a double exponential oxygen model (Equation 2.28, Section 2.3.6). This model was designed to decrease the bias towards the lower coordinated structures (i.e. the hexagonal P6₃cm) by biasing the minima in the interaction energy for the oxygen for larger separations. However, this potential model, did not improve the structure predictions either. The fact that only minor changes to the cation - anion interaction energy were made by the addition of the double exponential oxygen model can be seen by comparing the $Al^{3+}-O^{2-}$ interaction

energies shown in Figure 2.8(b).

Using the same logic, and following an approach which has previously proved successful for simulating hydroxides [65], a damped coulombic model was included (Equation 2.29, Section 2.3.6). As with the other potential models discussed thus far, this dampening of the coulombic interaction did not affect the interaction energies of the different coordinated systems enough to improved the structure or dielectric predictions to any noticeable degree.

A further change to the potential model was the addition of shells for the cations (Section 2.3.6). The values for the shell charge and spring constant were derived from work by Grimes and Grimes on the effective polarisability of a series of ions [53,54]. This shell model was developed for improvement of the dielectric constant predictions. Values of the dielectric constant were altered by using this model, however the fit to the experimental data for the aluminate materials was not improved.

3.7 Quantum Mechanical Structure Predictions

In an attempt to improve the structure predictions using a more rigorous approach, a subset of compositions were investigated further using quantum mechanical calculation. The compositions chosen were those at the boundaries between the different crystal structure types. The rationale being that only small adjustments of the structure predictions is necessary in order to improve the predictions based on pair potential calculations. The results of these calculations are presented in Table 3.11. Unfortunately only a small number of compositions could be investigated in this way due to the considerable computational effort. For the same reason, the garnet reaction has not been investigated due to the considerable size increase in the unit cell from the perovskite to garnet. The method is explained further in Chapter 2.

A plane wave cut-off of 480 eV was used, therefore these calculations are computationally intensive. In order to reduce the time taken per calculation the Brillouin zone was sampled at the gamma point. This work is still in progress and the results presented in this section are only preliminary.

 Table 3.11: Quantum mechanically calculated lattice energies for a subset of perovskite compositions.

Compound	Lattice Energy		
	$R\overline{3}c$	Pnma	$P6_3cm$
$PrAlO_3$	-2674.01659	-2674.73150	-
$NdAlO_3$	-2939.74107	-2941.73123	-
TbAlO_3	-	-4898.20138	-4909.45802
$DyAlO_3$	-	-5380.42850	-5386.74393
HoAlO_3	-	-5940.89595	-5944.40103
YbAlO ₃	-	-7791.63605	-7792.27850
$LuAlO_3$	-	-7158.39455	-7158.66758
$InAlO_3$	-	-2944.17758	-2944.65562
$LaInO_3$	-	-3754.64118	-3755.13198
$LaScO_3$	-	-3474.20790	-3474.22043

The results of the quantum mechanical calculations so far show that the Pnma symmetry is preferred over the $R\overline{3}c$ for $PrAlO_3$ and $NdAlO_3$ in agreement with pair potential predictions (Figure 3.10). Experiment, however, suggests that both should be $R\overline{3}c$ [102, 121].

For the remaining compositions (i.e. TbAlO_3 through to LaScO_3) these simulations suggest that the P6₃cm structure is more stable than the Pnma structure which is not always in agreement with the pair potential predictions. There is agreement with the pair potential predictions for the LaInO₃ which predict the P6₃cm structure. Unfortunately experimentally this compound has the Pnma structure [102]. For LaScO₃, the quantum mechanical lattice energy difference between the hexagonal and orthorhombic structures is very small which suggests this compound will be on the boundary between P6₃cm and Pnma phases. To this extent the pair potentials and quantum mechanics results agree in this case.

Discrepancies between the pair potentials and the quantum mechanics predictions are seen for the remaining compounds. For TbAlO₃, DyAlO₃, HoAlO₃, YbAlO₃, LuAlO₃ and InAlO₃, the quantum mechanics predicts that the hexagonal is the lowest energy structure yet the pair potentials only predict InAlO₃ to be hexagonal with the remainder being orthorhombic. Experimentally the structures are observed to be orthorhombic in agreement with pair potentials rather than quantum mechanics simulations.

The discrepancy in the quantum mechanical lattice energies may be due to the fact that calculations were performed for the gamma point only. This was to reduce the time constraints on the simulations, however further energy calculations are needed with a greater number of k points in an attempt to either improve or verify the quantum mechanical results.