Table 6.26: Calculated (using CASTEP) ^{89}Y NMR parameters, δ_{iso}, $\Delta\sigma_{CS}$ and η_{CS}, for composition $LaSc_{0.75}Y_{0.25}O_3$, where Y is substituted onto the B site.

	Site	δ_{iso} (ppm)	$\Delta\sigma_{CS}$ (ppm)	η_{CS}
$LaSc_{0.75}Y_{0.25}O_3$	Y1	430.0	−50.4	0.87

changed. For each of the compositions calculated a range of C_Q values were predicted for ^{45}Sc that varied from ~5 – 12 MHz, as shown in Table 6.27. It must be noted that several of the predicted values of C_Q were extremely large and would therefore result in very broad resonances. To determine whether any of the calculated compositions could, realistically, be observed experimentally the values obtained for each composition were 'summed', i.e., their contributions were added and a corresponding spectrum was simulated. The spectrum produced is shown (in blue) in Figure 6.30. Rather surprisingly, when compared with the broad ^{45}Sc MAS NMR spectra obtained for samples in the $La_{1-x}Y_xScO_3$ series (Figure 6.17) relatively good agreement was observed in both the position (shifted upfield from $LaScO_3$) and the shift range observed. This suggests all possible compositions simulated using DFT methods are potentially present in each of the samples synthesised.

The ^{89}Y NMR parameters calculated for each composition described above indicated a range of chemical shifts, as shown in Table 6.28. To determine whether any of these shifts were feasible experimentally NMR spectra for each were simulated and compared with the observed experimental resonances. Tick marks corresponding to each of the predicted Y sites have been added to the ^{89}Y MAS NMR spectrum of $La_{0.6}Y_{0.4}ScO_3$, and are shown in Figure 6.31. Each of the predicted sites appear close to one another, highlighting the range of shifts exhibited. This range predicted using DFT methods resides under the experimental lineshape and therefore suggests that each one could be observed experimentally. Good agreement was therefore observed between experiment and the calculated values.

In reality, to gain further insight into the disorder exhibited DFT calculations using much larger cells are required. Using the supercell

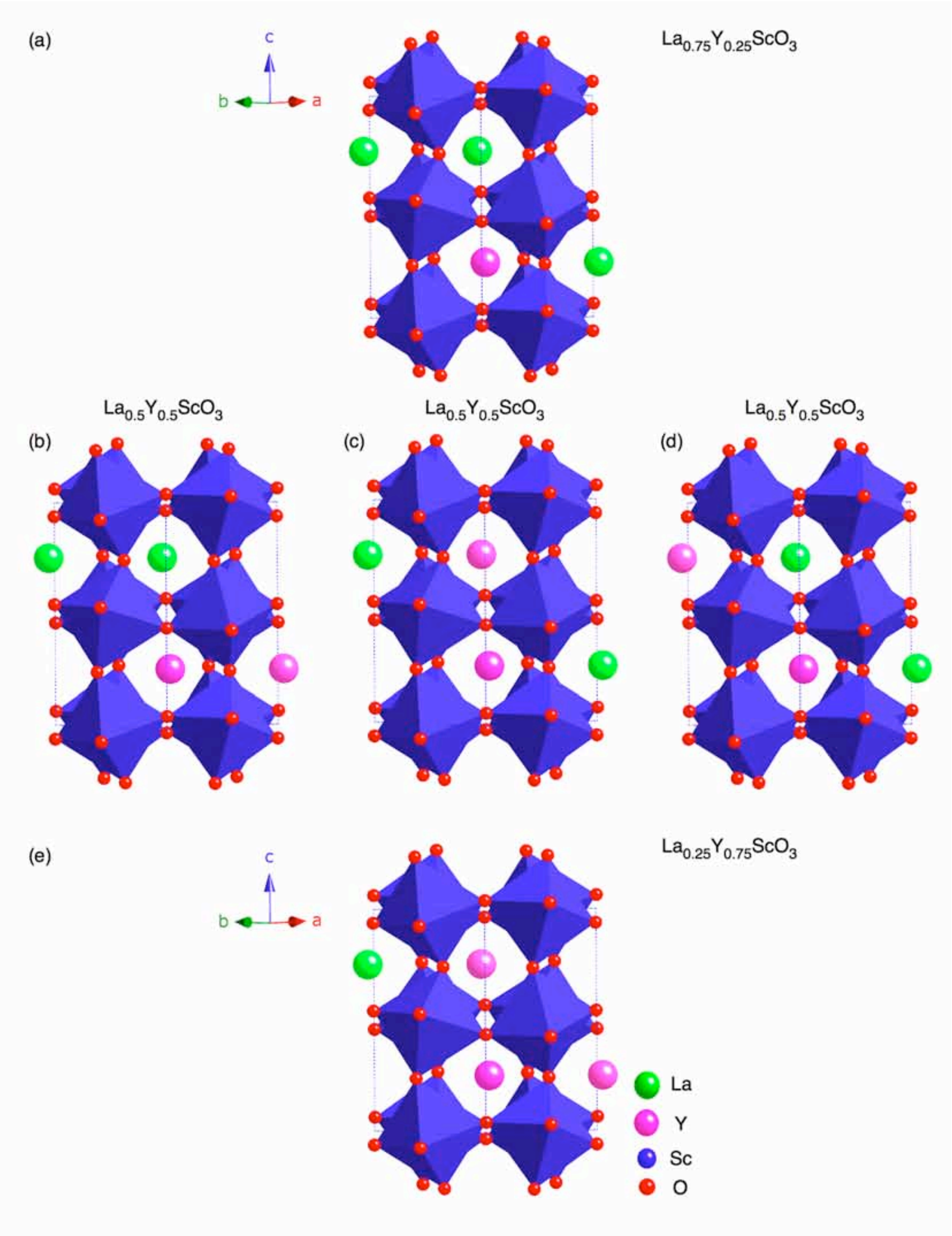

Figure 6.29: The structures of (a) $La_{0.75}Y_{0.25}ScO_3$, (b-d) $La_{0.5}Y_{0.5}ScO_3$ and (e) $La_{0.25}Y_{0.75}ScO_3$ used to gain insight into the disorder exhibited in the $La_{1-x}Y_xScO_3$. Each structure was geometry optimised prior to calculation of the ^{45}Sc and ^{89}Y NMR parameters given in Tables 6.27 and 6.28.

Table 6.27: Calculated (using CASTEP) ^{45}Sc NMR parameters, δ_{iso}, P_Q, C_Q and η_Q, for x = 0, 0.25, 0.5, 0.75 and 1 in the series $La_{1-x}Y_xScO_3$. The initial $LaScO_3$ structure was obtained from literature.[218] To 'model' disorder Y atoms were placed on different La sites, structures were then relaxed and subsequent NMR parameters were calculated, as described in Appendix V.

	Site	δ_{iso} (ppm)	P_Q / MHz	C_Q / MHz	η_Q
$La_{0.75}Y_{0.25}ScO_3$	Sc1	159.2	7.82	7.62	0.40
	Sc2	164.9	−5.15	−4.64	0.83
$La_{0.5}Y_{0.5}ScO_3$ (A)	Sc1	159.8	7.46	6.59	0.92
$La_{0.5}Y_{0.5}ScO_3$ (B)	Sc1	156.7	12.29	12.03	0.36
	Sc2	164.8	9.13	8.25	0.82
$La_{0.5}Y_{0.5}ScO_3$ (C)	Sc1	162.3	5.52	4.8	0.98
$La_{0.25}Y_{0.75}ScO_3$	Sc1	157.7	9.99	9.76	0.38
	Sc2	160.2	−8.07	−7.77	0.49

approximation and the inherent periodic boundary conditions of each system, the structure can be extended in all three dimensions by a greater number of unit cells. A 2 × 2 × 2 supercell therefore extends the structure in three dimensions by an additional unit cell. Calculations of this type are, however, computationally demanding and often require large computational resources. To determine the feasibility of completing supercell calculations using the computational resources currently available to us a 2 × 1 × 1 supercell calculation was completed. Initially a single La atom was replaced in the 2 × 1 × 1 cell with Y, producing the composition $La_{0.875}Y_{0.125}ScO_3$, shown in Figure 6.32(a). In a similar manner to earlier calculations, the structure was geometry optimised prior to calculation of the NMR parameters. The calculated ^{45}Sc and ^{89}Y NMR parameters can be found in Table 6.29 and 6.30, respectively. For example, geometry optimisation calculations can take from between two

Table 6.28: Calculated (using CASTEP) ^{89}Y NMR parameters, δ_{iso}, $\Delta\sigma_{CS}$ and η_{CS}, for x = 0, 0.25, 0.5, 0.75 and 1 in the series $La_{1-x}Y_xScO_3$. The initial $LaScO_3$ structure was obtained from literature.[218] To 'model' disorder Y atoms were placed on different La sites, structures were then relaxed and subsequent NMR parameters were calculated, as described in Appendix V.

	Site	δ_{iso} (ppm)	$\Delta\sigma_{CS}$/ ppm	η_{CS}
$La_{0.75}Y_{0.25}ScO_3$	Y1	234.8	−136.8	0.57
$La_{0.5}Y_{0.5}ScO_3$ (A)	Y1	229.1	−131.1	0.75
$La_{0.5}Y_{0.5}ScO_3$ (B)	Y1	246.4	−156.0	0.38
$La_{0.5}Y_{0.5}ScO_3$ (C)	Y1	255.5	−124.7	0.14
$La_{0.25}Y_{0.75}ScO_3$	Y1	242.2	−150.9	0.52
	Y2	247.7	−121.0	0.44
	Y3	267.5	−140.6	0.17

and seven days to complete using 20 processors. Calculations were also attempted, substituting two La atoms in the 2 × 1 × 1 supercell with Y, producing the composition $La_{0.75}Y_{0.25}ScO_3$. Note that there were several possible ways in which to complete this particular substitution. Shown in Figure 6.32(b) and (c) are the two methods of substitution used for this particular composition. Again, each structure was optimised prior to calculation of the NMR parameters to ensure each structure was in a local energy minimum. The calculated ^{45}Sc NMR parameters for the two structures are given in Table 6.29. The number of sites predicted again varied as a function of symmetry. As observed for earlier single cell calculations, a large range of values of C_Q (~4 – 14 MHz) were predicted for each of the ^{45}Sc sites. The contribution from each of these sites was also summed and the spectrum obtained is shown (in purple) in Figure 6.30. The simulated spectrum again highlights that each composition calculated could be present in each sample experimentally. Also shown in Figure 6.30, and denoted in green, is the summation of the two simulated spectra.

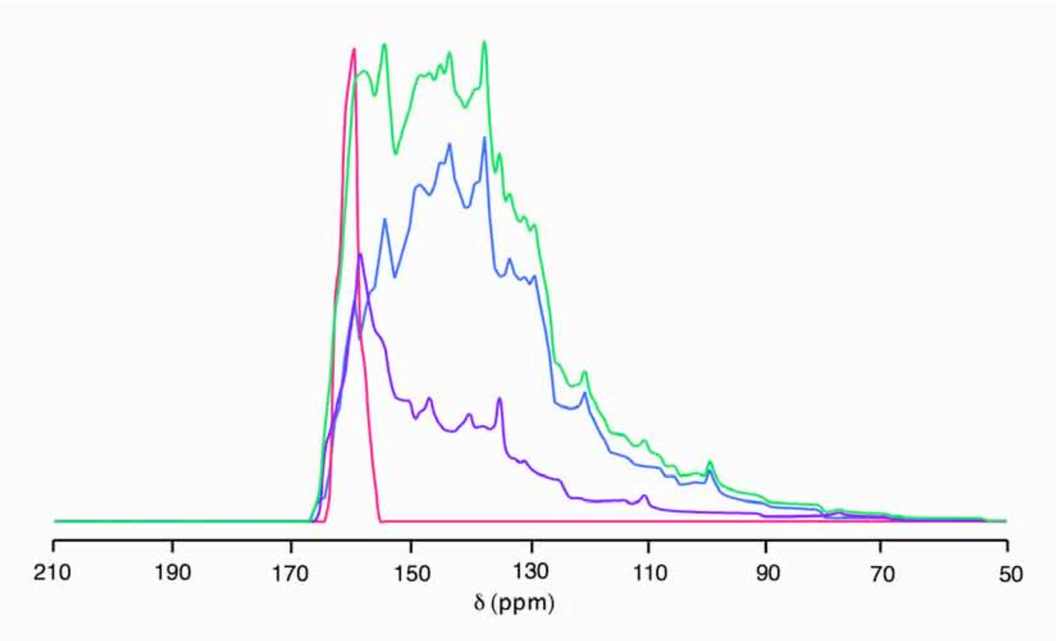

Figure 6.30: Simulated ^{45}Sc MAS NMR spectra obtained by 'summing' the NMR parameters obtained from the ^{45}Sc DFT calculations completed for a single unit cell (1 × 1 × 1), shown in blue, and a 2 × 1 × 1 supercell, shown in purple. Also shown in green is the summation of the two simulated patterns.

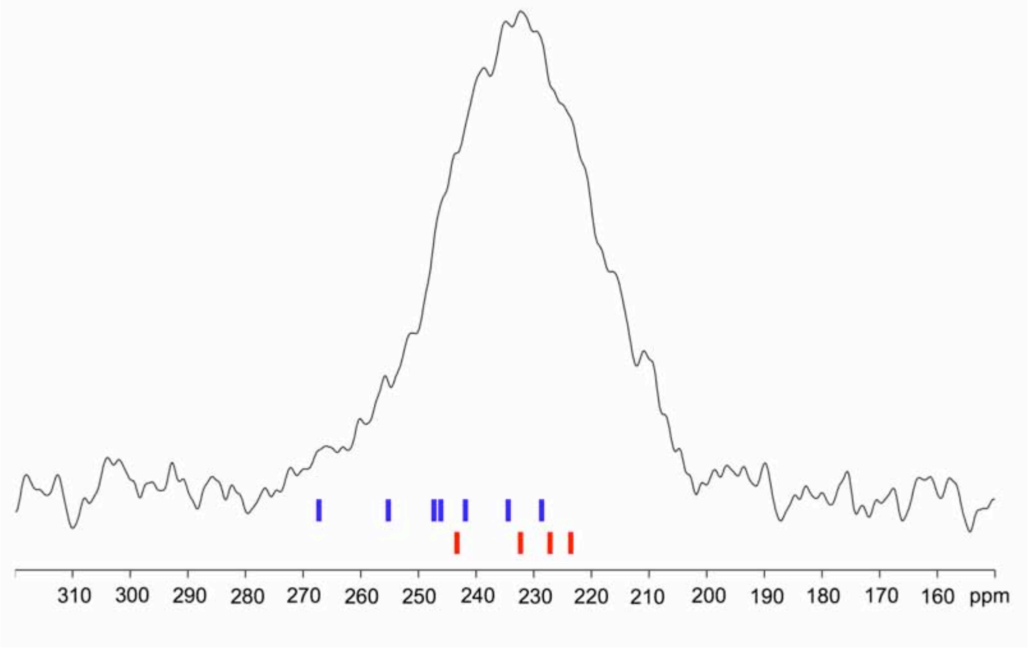

Figure 6.31: The ^{89}Y (14.1 T) MAS NMR spectrum of $La_{0.6}Y_{0.4}ScO_3$ (see Figure 6.22) with tick marks corresponding to the calculated chemical shifts of Y sites in a 1 × 1 × 1 single cell (shown in blue) and 2 × 1 × 1 supercell (shown in red) calculations.

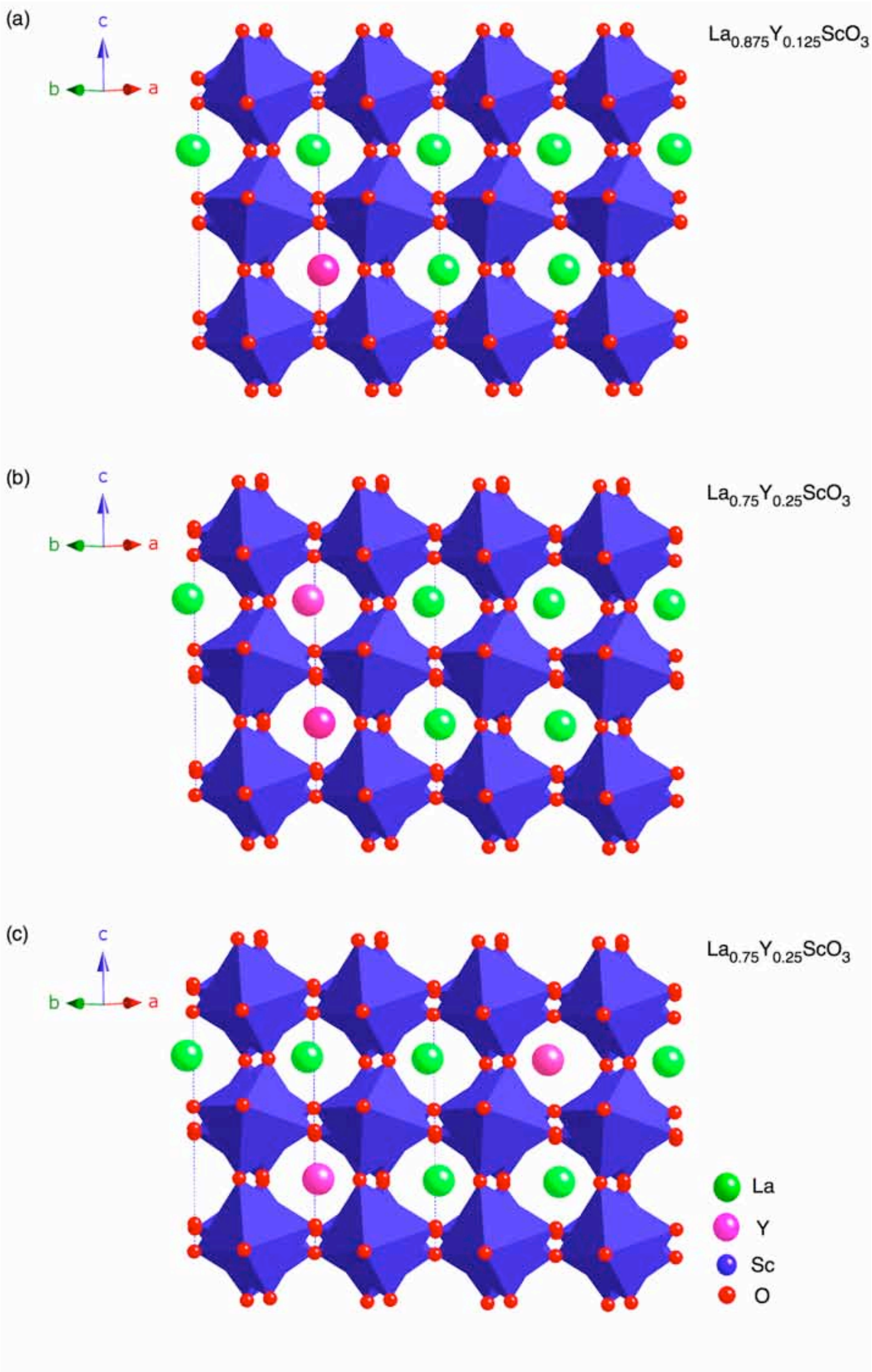

Figure 6.32: The structures of (a) $La_{0.875}Y_{0.125}ScO_3$ and (b-c) $La_{0.75}Y_{0.25}ScO_3$ used to calculate the NMR parameters in a 2 × 1 × 1 supercell. Each structure was geometry optimised prior to calculation of the ^{45}Sc and ^{89}Y NMR parameters given in Tables 6.29 and 6.30.

Table 6.29: Calculated (using CASTEP) ^{45}Sc NMR parameters, δ_{iso}, P_Q, C_Q and η_Q, for compositions x = 0.125 and 0.25. To 'model' disorder Y atoms were placed on different La sites in the $LaScO_3$ structure obtained for the literature.[218] All structures were relaxed prior to the NMR parameters being calculated.

	Site	δ_{iso} (ppm)	P_Q / MHz	C_Q / MHz	η_Q
$La_{0.875}Y_{0.125}ScO_3$	Sc1	158.6	8.58	8.48	0.26
	Sc2	163.4	−4.63	−4.39	0.58
	Sc3	163.1	−4.22	−3.79	0.85
	Sc4	163.6	−6.58	−6.06	0.73
$La_{0.75}Y_{0.25}ScO_3$ (A)	Sc1	155.2	13.66	13.62	0.13
	Sc2	163.6	−4.65	−4.05	0.98
	Sc3	163.7	−5.73	−5.05	0.93
	Sc4	163.1	−4.82	−4.25	0.93
$La_{0.75}Y_{0.25}ScO_3$ (B)	Sc1	159.6	8.34	8.06	0.46
	Sc2	164.8	−8.07	−7.99	0.25
	Sc3	163.4	−11.90	−11.58	0.41

The same upfield shift from $LaScO_3$ is observed and good agreement in the linewidth is also observed. Similar ^{89}Y NMR calculations were also completed for each composition, details of which are given in Table 6.30. As previously observed for the single cell calculations, a range of chemical shifts were predicted. To illustrate whether any of these sites could be observed experimentally in the $La_{1-x}Y_xScO_3$ series, tick marks corresponding to each shift have been added to the ^{89}Y MAS NMR spectrum for the x = 0.4 sample, and are shown in red in Figure 6.31. The range of chemical shifts is relatively small and realistically each site could reside under the experimental lineshape, as highlighted in Figure 6.31.

Unfortunately, it was not possible to complete any larger supercell calculations as our computational resources are, at present, limited. In reality, to complete calculations of this nature greater computational resources would be required. However, the calculations completed have

Table 6.30: Calculated (using CASTEP) ^{89}Y NMR parameters, δ_{iso}, $\Delta\sigma_{CS}$ and η_{CS}, for compositions x = 0.125 and 0.25. To 'model' disorder Y atoms were placed on different La sites in the $LaScO_3$ structure obtained for the literature.[218] All structures were relaxed prior to the NMR parameters being calculated.

	Site	δ_{iso} (ppm)	$\Delta\sigma_{CS}$ / ppm	η_{CS}
$La_{0.875}Y_{0.125}ScO_3$	Y1	230.6	−129.5	0.24
$La_{0.75}Y_{0.25}ScO_3$ (A)	Y1	239.3	−142.1	0.22
	Y2	234.1	−144.1	0.26
$La_{0.75}Y_{0.25}ScO_3$ (B)	Y1	250.4	−142.8	0.21

provided valuable insight into the possibility of modelling disorder using DFT calculations.

6.4 Conclusions

In summary, we have successfully synthesised and characterised the solid-solution $La_{1-x}Y_xScO_3$ for compositions x = 0, 0.2, 0.4, 0.6, 0.8 and 1 using high-resolution neutron powder diffraction, solid-state NMR and DFT calculations. All samples in this series were found to be orthorhombic and isostructural with $GdFeO_3$, in space group Pbnm. As Y was gradually introduced to the $LaScO_3$ structure a corresponding decrease in both the lattice parameters and unit cell volume was observed. In addition, as x was increased the degree of orthorhombic strain placed on the structure gradually increased and, as a direct consequence, the tilt angle(s) observed for the ScO_6 octahedra steadily increased. Structurally, only minor changes in the Sc – O bond lengths were observed as x was increased. As the level of strain gradually increased with x a substantial effect on the magnitude of the quadrupolar interaction was observed.

^{45}Sc MAS NMR was shown to be highly sensitive to substitutions occurring on the A site. In contrast, the ^{89}Y MAS NMR completed indicated the Y environment to be less sensitive to changes on the A site. The Sc – La/Y distances are shorter than the La – La/Y distances. The local environment of the Sc is therefore severely affected by cation substitution on the A site owing to the close proximity of the Sc to a substituted La atom. Each sample in the series $La_{1-x}Y_xScO_3$ was shown to exhibit disorder and using two-dimensional ^{45}Sc MAS NMR techniques and it was found to result from both a distribution of quadrupoles and chemical shifts. Using ^{45}Sc, ^{89}Y MAS NMR in conjunction with high-resolution NPD data the greatest disorder is believed to be in compositions close to x = 0.5 in the solid-solution $La_{1-x}Y_xScO_3$.

In addition, we have successfully implemented ^{45}Sc, ^{89}Y and ^{17}O DFT calculations using CASTEP for $LaScO_3$, $YScO_3$ and a series of model compounds, the results of which displayed very good agreement with those obtained experimentally. Several additional calculations were completed in an attempt to provide insight into the disorder exhibited in the $La_{1-x}Y_xScO_3$ solid-solution. Initial calculations were successful and suggested a variety of different compositional environments could be present in each sample. It is highly likely that, experimentally, a 'summation' of all the calculated environments is observed. The preliminary calculations completed therefore suggest that 'modelling' disorder using DFT could aid considerably in the understanding and interpretation of complex NMR spectra of disordered materials.

Also in this investigation we have managed to successfully enrich $LaScO_3$ using $^{17}O_2$ enriched gas, suggesting post-synthetic enrichment of dense perovskite-based compounds is feasible. This, in turn, suggests it would be highly advantageous to enrich disordered samples and probe the local oxygen environment using ^{17}O MAS NMR in an attempt to gain insight into the nature and extent of the disorder exhibited. Finally, we emphasise the importance of using a multidisciplinary approach to the structural investigation of complex solid-state systems such as $La_{1-x}Y_xScO_3$. Using a variety of highly complementary techniques it is possible to gain important additional structural information that may be lost by the use of a one technique alone.

Chapter 7
Conclusions and Future Work

7.1 Conclusions

The primary focus of this thesis was to synthesise and characterise several perovskite systems using high-resolution powder diffraction, solid-state NMR and first-principles DFT calculations.

Initial investigations concentrated on $NaNbO_3$ at room temperature and the work presented has shown that laboratory-synthesised samples of $NaNbO_3$ routinely comprise of two structurally very similar orthorhombic phases; the centrosymmetric Pbcm and polar $P2_1ma$ polymorphs. In addition, the quantity of each phase present has been shown to vary as a function of the preparative method. It was possible to synthesise a phase pure sample of Pbcm $NaNbO_3$ using molten salt techniques. However, it was considerably harder to synthesise a phase pure sample of the $P2_1ma$ polymorph, as small quantities of the more thermodynamically stable Pbcm phase were consistently produced. Using high-resolution s-PXRD and NPD data it was possible to distinguish between the two phases. Close examination of the superstructure peaks in each dataset proved key in identifying precisely which phase(s) were present in each sample. Using conventional and two-dimensional solid-state NMR techniques it was only possible to distinguish between the Pbcm and $P2_1ma$ phases using ^{23}Na MQMAS NMR. The ^{93}Nb MAS and static NMR spectra appeared virtually identical for the two phases, indicating the Nb environment to be very similar in each. Using $^{17}O_2$ gas it was possible to post-synthetically enrich selected samples of $NaNbO_3$. However, considerable spectral overlap was observed in each ^{17}O MAS NMR spectrum owing to the extreme similarities of sites O1 and O2, and sites O3 and O4 in both the Pbcm and $P2_1ma$ phases. The spectral overlap exhibited confirmed previous conclusions drawn from ^{23}Na and ^{93}Nb MAS NMR as to the very similar nature of the two $NaNbO_3$ polymorphs.

The ^{23}Na, ^{93}Nb and ^{17}O DFT calculations completed for the different phases of $NaNbO_3$ displayed very good agreement with the observed experimental findings. In particular, the ^{17}O DFT calculations aided in confirming the spectral assignment initially made using published crystallographic data. Using AIRSS, structure searching methods were also employed for $NaNbO_3$ and, consistently, the most energetically favourable phases of $NaNbO_3$ found were the R3c, Pmc2_1 (i.e., P2_1ma) and Pbcm phases. This was in good agreement with the observed experimental findings. The structure searching results obtained were extremely encouraging as they suggest that this method could be utilised with similar success for many other perovskite-based systems in the future.

Using ^{23}Na MQMAS techniques a third, unknown Na-based phase was consistently found in all samples of $NaNbO_3$ investigated, including the commercially purchased sample. However, owing to the exceptionally small quantities of this phase present in each sample (~1-2%) it was not possible to identify its presence in any diffraction pattern and, as a result, the phase could not be successfully characterised.

The effect of low percentage doping was investigated in the $NaNbO_3$-related solid-solutions KNN (1-5%), LNN (1-10%) and SNN (10-40%) and, in most cases, the P2_1ma polymorph of $NaNbO_3$ was formed. Associated changes in both the lattice parameters and unit cell volume were observed as each cation was substituted into the $NaNbO_3$ structure. The substitution of K^+ and Li^+ cations into the $NaNbO_3$ structure appears to result in a structural distortion which results in the loss of the antiphase tilts responsible for the antiferroelectric fourfold superstructure of the Pbcm phase, and subsequently produces the P2_1ma phase. The introduction of vacancies and, in particular, the concentration of [Sr-vacancy] in the SNN solid-solution is believed to play a crucial role in determining the phases formed. Disorder was identified in each series, believed to be primarily owing to a distribution of chemical shifts.

The low temperature s-PXRD study completed for the sol-gel sample of $NaNbO_3$ identified a region of phase coexistence between the P2_1ma, R3c and Pbcm phases of $NaNbO_3$ over a relatively large temperature range, 12 < T < 280 K. The observed phase coexistence was in good agreement with earlier NPD studies completed by Mishra *et al.*,[224] in which a two phase region of coexistence was identified between the Pbcm and R3c phases. It is believed that to achieve full conversion of the $P2_1ma$ and/or Pbcm phases of $NaNbO_3$ to the low temperature R3c phase each sample would need to remain at low temperatures for a substantial period of time. The time taken to complete the low temperature s-PXRD study was therefore insufficient to adequately cool the entire sample and achieve full conversion to the low temperature phase.

The compositions x = 0, 0.2, 0.4, 0.6, 0.8 and 1 in the solid-solution $La_{1-x}Y_xScO_3$ were successfully synthesised and characterised. All samples were found to be isostructural with $GdFeO_3$ and refined NPD data indicated that an orthorhombic structure was retained throughout the solid-solution, in space group Pbnm. The structure of the end member, $YScO_3$, was correctly ascertained for the first time by structural refinement of high-resolution NPD data using the Rietveld method. This was completed using $HoScO_3$[218] as the initial model and lattice parameters estimated by Clark *et al.*[298] A gradual decrease in the lattice parameters and unit cell volume was observed with increasing x. The degree of orthorhombic strain and the tilt angle(s) observed for the ScO_6 octahedra steadily increased with x. Using ^{45}Sc and ^{89}Y NMR each sample in the series was found to exhibit disorder. Using ^{45}Sc MAS NMR the disorder was found to result from both a distribution of quadrupoles and chemical shifts. The sample $La_{0.6}Y_{0.4}ScO_3$ was found to exhibit the greatest degree of disorder, confirmed both by the NPD and NMR data obtained. The ^{45}Sc MAS NMR data indicates that Sc NMR parameters are highly sensitive to cation substitutions on the A site. In contrast, the ^{89}Y MAS NMR data suggests yttrium shift is less sensitive to substitution on the A site, most probably owing to the large distance between two A-site cations. The findings presented do, however, suggest that the Y environment would experience a much greater effect if substitution was to occur on the B site. A sample of the end-member, $LaScO_3$, was post-synthetically enriched using $^{17}O_2$ gas and subsequently investigated using ^{17}O NMR. The ^{17}O MAS NMR spectrum obtained for $LaScO_3$ displayed two resonances, in good agreement with published crystallographic data. Very small values of C_Q were exhibited for each site, indicating two highly symmetrical oxygen environments. This, therefore, indicates that the post-synthetic enrichment of dense perovskite phases such as $LaScO_3$ is feasible and could potentially be applied to many other perovskite phases. In particular, enrichment of disordered perovskites would be hugely informative as this would aid in identifying any subtle differences exhibited in the different oxygen environments. ^{45}Sc, ^{89}Y and ^{17}O DFT calculations were also carried out for the end-members, $LaScO_3$ and $YScO_3$ and the results obtained indicated very good agreement with the experimental findings. Furthermore, to gain insight into disorder several calculations were attempted in which different La atoms in the unit cell were substituted with Y to produce compositions $La_{0.75}Y_{0.25}ScO_3$, $La_{0.5}Y_{0.5}ScO_3$ and $La_{0.25}Y_{0.75}ScO_3$. This proved highly successful and when the contribution from each was 'summed' and a spectrum was simulated, good agreement was observed with experiment, indicating that each of the calculated environments could realistically be found experimentally. This result is particularly encouraging as it suggests that similar and more complex methods such as supercells could be adopted and utilised to investigate other disordered materials.

The work presented in this thesis has demonstrated the effectiveness of combining three very powerful techniques. Furthermore, this work has highlighted the importance of using a multidisciplinary approach for the investigation of structurally complex systems. Using a single characterisation technique it is often difficult to gain an accurate and robust structural characterisation. Therefore, it is often better to utilise a variety of different techniques to gain a complete and comprehensive structural solution to the system under investigation.

7.2 Future Work

Although a largely exhaustive and comprehensive study has been completed for each of the systems investigated, several additional areas of interest and future investigation still remain. For example, it would be beneficial to accurately charcterise the 'third phase' consistently present in all samples of $NaNbO_3$ as this could potentially provide additional information regarding the formation of the different phases of $NaNbO_3$. This could, in turn, provide further insight into the $NaNbO_3$ system. However, to do so, a sample composed of principally this phase is needed. Therefore, a systematic study of reaction conditions is necessary to identify the exact synthetic method required to synthesise such a sample. Once known, a sample could be synthesised and using a combination of high-resolution NPD and ^{23}Na MQMAS NMR techniques it would be possible to characterise this phase.

The KNN and LNN solid-solutions possesses additional NMR active species, namely ^{39}K (I = 3/2), ^{7}Li (I = 3/2) and ^{17}O (I = 5/2). It would be particularly useful to complete ^{39}K and ^{7}Li NMR studies on the KNN and LNN series as each could potentially provide additional, complementary, information regarding the A site environment in each. Furthermore, ^{17}O enrichment of each sample in both series could, potentially, aid in interpreting the disorder exhibited in each sample.

Within this particular invstigation no NMR studies were completed for samples in the SNN series owing, principally, to large quantities of an impurity phase in each. The initial diffraction studies completed suggest that this may be an interesting series to study by NMR. However, phase pure samples would be required before any detailed studies could be completed. Hence, a thorough investigation of the synthesis conditions required to synthesise phase pure samples is necessary. Many of the samples in the KNN, LNN and SNN series were found to comprise of the same polar, and potentially ferroelectric, $P2_1ma$ phase. Therefore, it would be particularly interesting to assess the magnitude of the piezoelectric responses exhibited by samples in each series. Dielectric measurements of each sample are therefore required.

The low temperature study completed for the sol-gel sample of $NaNbO_3$ indicated that at low temperatures a mix of three phases was exhibited. Given these findings, it would be interesting to determine whether any similar regions of phase coexistence are exhibited at high temperatures. We recently completed a preliminary high temperature study using NPD for the sol-gel sample of $NaNbO_3$ and initial results appear promising. We have also recently been allocated beamtime at I11 to complete a more comprehensive high temperature study on the sol-gel sample of $NaNbO_3$. It is hoped that this will aid in confirming the preliminary results obtained from the NPD data. In addition, it would be highly informative to complete low temperature ^{23}Na and ^{93}Nb NMR studies. This would aid in confirming the findings already obtained from the low temperature diffraction study completed.

The structural characterisation completed for the solid-solution $La_{1-x}Y_xScO_3$ was comprehensive. However, a number of minor areas of investigation still remain. For example, it would be advantageous to ^{17}O enrich all remaining samples in the series as this could, potentially, provide additional information regarding the disorder exhibited in the system. Furthermore, it would be highly desirable to complete a 2 × 2 × 2 supercell calculation to determine whether computational methods can provide any additional insight into the disorder exhibited experimentally. However, to feasibly undertake such a calculation, access to large computational resources would be required. The preliminary calculations completed to date suggest that a calculation of this magnitude would require a large amount of computational time. However, if this could be achieved the results obtained could potentially aid in confirming initial conclusions drawn from the single cell calculations that all possible environments calculated could feasibly be present in each sample.

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