A Computational Investigation of NMR Properties of Mixed-Metal Niobate Perovskites

Rebecca Bisset

rb254@st-andrews.ac.uk

Ashbrook Group, School of Chemistry, University of St Andrews

University of St Andrews

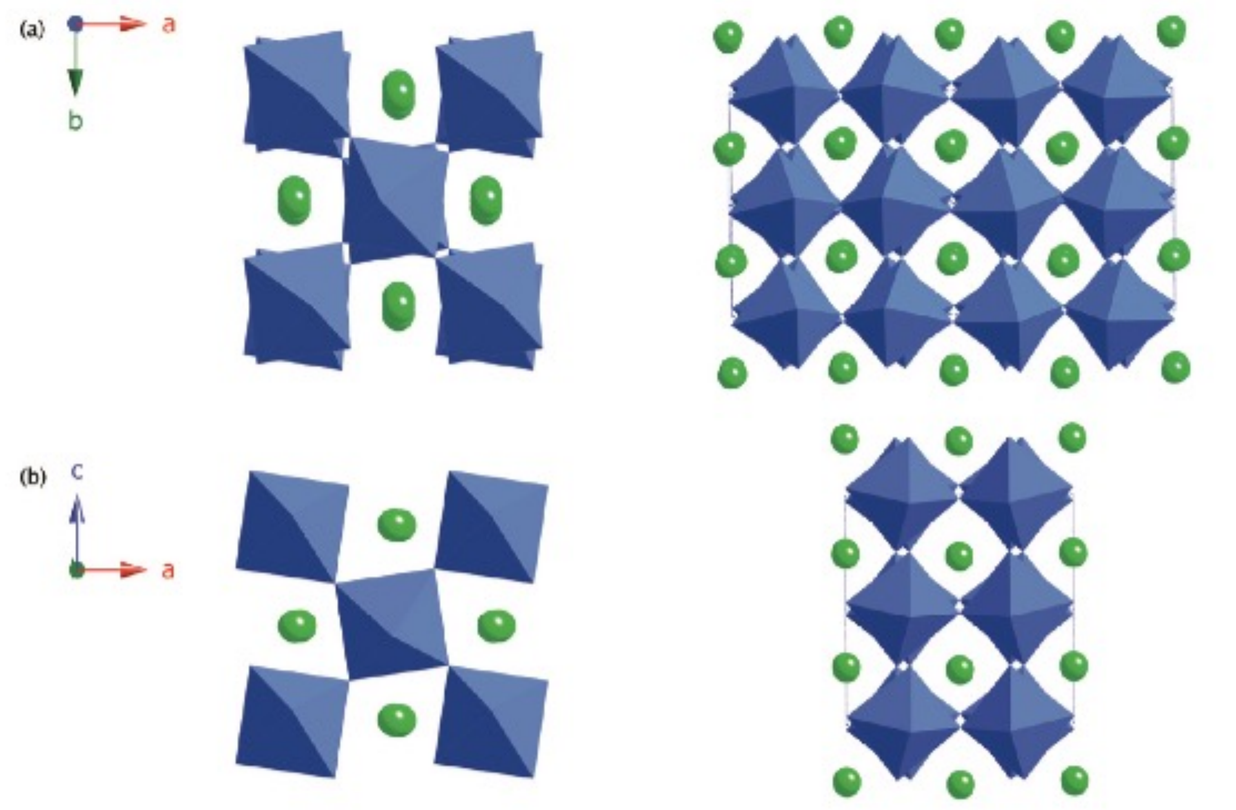
Introduction

Perovskites are a family of materials with the formula ABX_3 with wide-ranging properties and applications which have brought them much scientific interest. Niobate-based perovskites show promising electronic properties – such as ferroelectricity and piezoelectricity – leading to many applications from optical storage to sensors and actuators. Sodium niobate ($NaNbO_3$) derivatives – particularly $K_xNa_{1-x}NbO_3$ solid solutions – are very promising candidates to replace $Pb(Zr,Ti)O_3$ piezoelectrics, providing an effective yet non-toxic alternative.[1]

In solid solutions, the level of disorder is high and so NMR analysis is the favoured analytical technique, as it is sensitive to atomic-range disorder. The low natural abundance of ^{17}O, 0.038%, means that to yield experimental results, costly oxygen-enrichment must be carried out.[2] The alternative to this is the use of computation to simulate these results for different compositions of the solid solutions, and thus provide a precursor for later, more-focused, experimentation.

In this research, the *Pbcm* and *P2₁ma* polymorphs of $NaNbO_3$ and $KNbO_3$ (*Amm2*) are used to create solid solutions of $K_xNa_{1-x}NbO_3$ – allowing experimental results to be compared to several variations of each configuration.

This research utilizes density functional theory (DFT) which builds an energy function for a structure based upon the total electron density and the positions of the electrons within the structure.



Crystal structures of (a) *Pbcm* and (b) *P2₁ma; Green spheres represent Na atoms and blue octahedra represent NbO₆ octahedra.*[3]

Methodology

The initial end member structures were obtained from the Inorganic Crystal Structure Database. The Site Occupancy Disorder (SOD)[4] program was then used to carry out ensemble-based modelling on the end members in order to generate intermediate substitutions of the solid solutions – namely the x = 0.5 structures, since these could not simply be done by hand – and produce supercells so that each structure was a Z=8 supercell.

CASTEP code was used to carry out the DFT calculations on the perovskite structures using gauge including projector augmented waves (GIPAWs),[5] and the generalized gradient approximations PBE and PBEsol were used as the functionals.[6,7] The Brioullin space was sampled using a k-point spacing of 0.04 $Å^{-1}$, and the cut-off energy for the planewaves used to approximate each wavefunction was set as 60 Ry. These parameters were chosen by carrying out a convergence test of the energy values of $NaNbO_3$ while varying the two parameters. PBE and PBEsol were compared by optimizing the three initial end members and then running NMR calculations, both using each functional so that four sets of results were gained and could be compared. After this, the PBE functional was used for both optimization and NMR calculations.

Each structure was optimized, and NMR calculations carried out, both using the PBE functional and parameters mentioned above. The CASTEP NMR calculations yield values for the isotropic shielding, σ_{iso}, the magnitude of quadrupolar interaction, C_Q, and quadrupolar interaction asymmetry η_Q, and so for comparison to experimental results σ_{iso} must be converted to δ_{iso}:

$$\delta_{iso} = -(\sigma_{iso} - \sigma_{ref})$$

σ_{ref} is the reference isotropic shielding. σ_{ref} values were calculated using the ilmenite polymorph of $NaNbO_3$ and cristobalite (559.7 ppm for ^{23}Na, 261.5 ppm for ^{17}O, respectively).

PBE vs. PBEsol

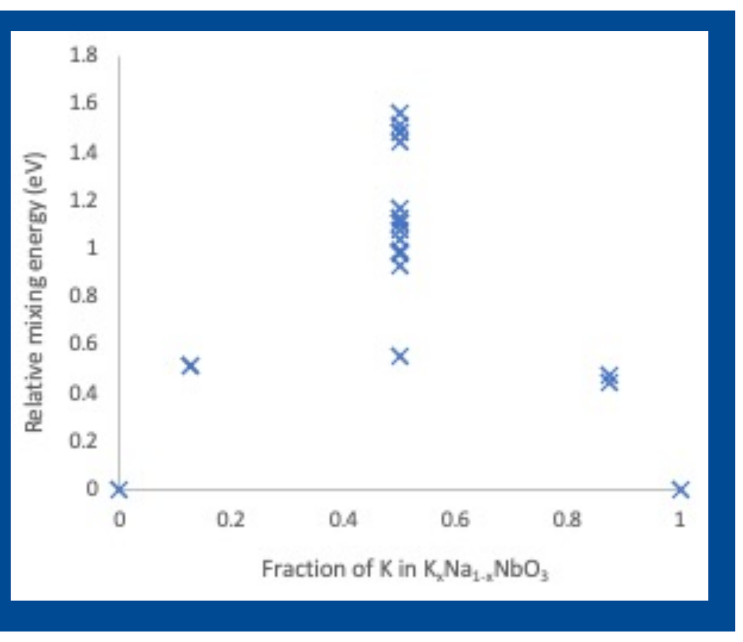
A preliminary investigation of the PBE and PBEsol functionals was carried out using the three initial end members. Cell parameters, bond lengths and NMR parameters were all compared using a combination of PBE and/or PBEsol to optimise and calculate NMR results. The two functionals performed similarly, with PBE slightly outperforming PBEsol. This, combined with the lesser computational time needed for PBE-only calculations, led to a decision to use PBE as the sole functional in the further analysis.

Relative Mixing Energies

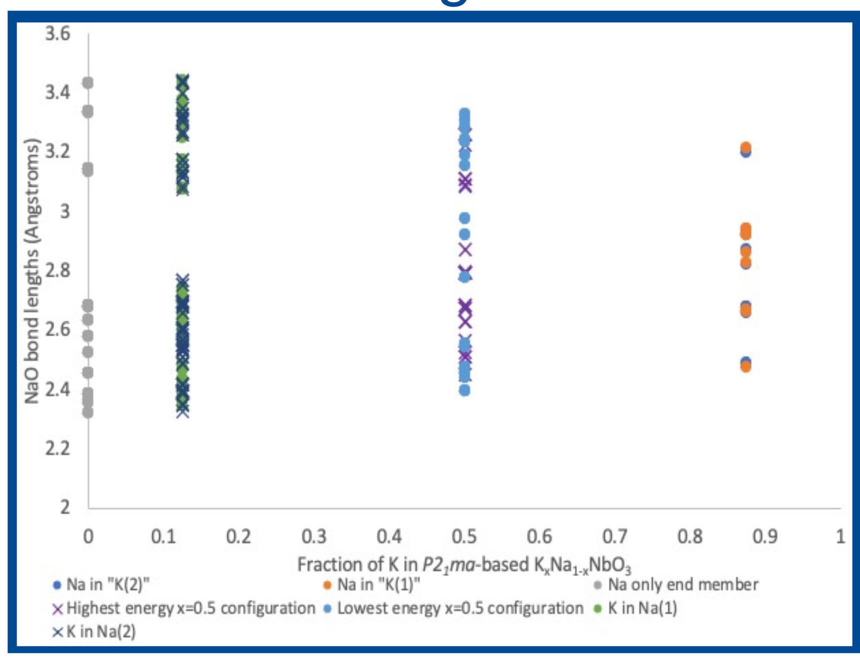
The relative mixing energies of the three sets of solid solutions were calculated by comparing the energy value predicted by CASTEP to the theoretical mixing energy (found using the energies of the end members of each set in the proportion dictated by the solid solution).

For all three polymorph-based sets, the relative mixing energies upon substitution into the end members were positive – meaning the formation of solid solution was unfavourable relative to the end members.

The figure here shows the relative mixing energy results for the *Pbcm*-based set of solid solutions.



NaO Bond Lengths



$NaNbO_3$ would have NaO_{12} coordination in an ideal perovskite. The bond length of Na-O in these perovskite structures can be predicted to be 2.79 Å, using the ionic radii of Na^+ and O^{2-}.[8]

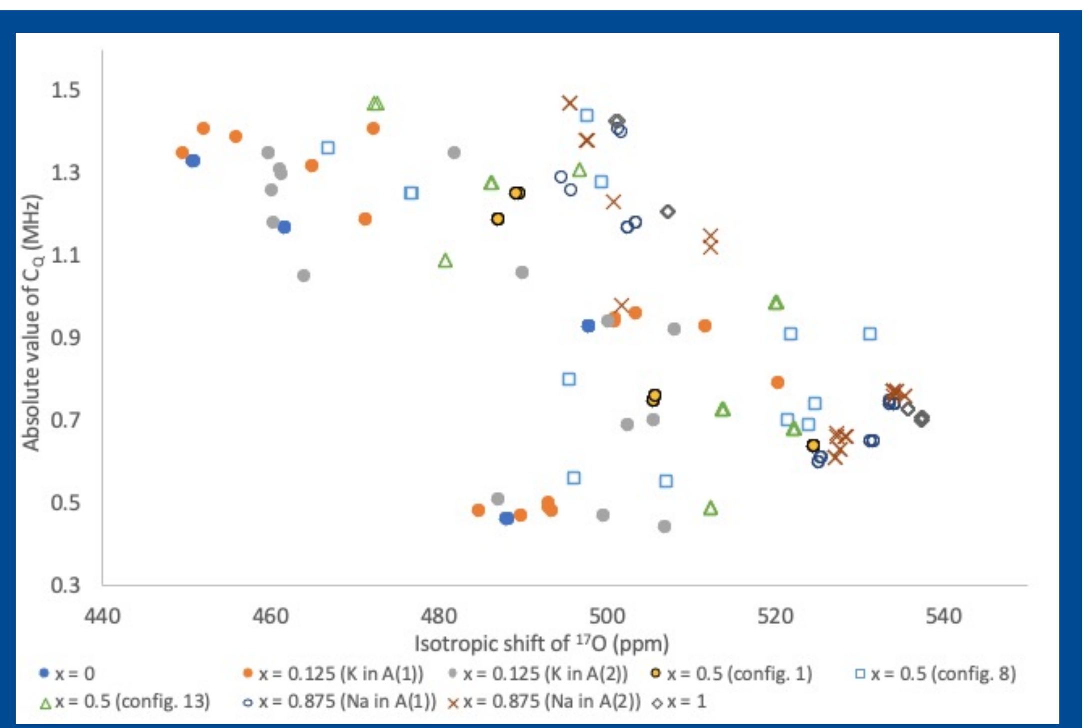
The *Pbcm*- and *P2₁ma*-based results showed two groups of bond lengths (<3 Å and >3 Å, separated by ~0.3 Å) which, considering the predicted bond length of 2.79 Å, may show the cut off of the coordination. This suggests that the ideal NaO_{12} perovskite structure is not achieved in these niobates – based upon these bond lengths the true coordination may be NaO_7 to NaO_9 for the $NaNbO_3$ end member, depending on the polymorph.

NMR Parameters

NMR calculations were run on each structure produced and compiled. CASTEP produces NMR results for all the relevant nuclei (here ^{17}O, ^{23}Na, ^{39}K and ^{93}Nb), but the analysis is focused on the ^{17}O and ^{23}Na results.

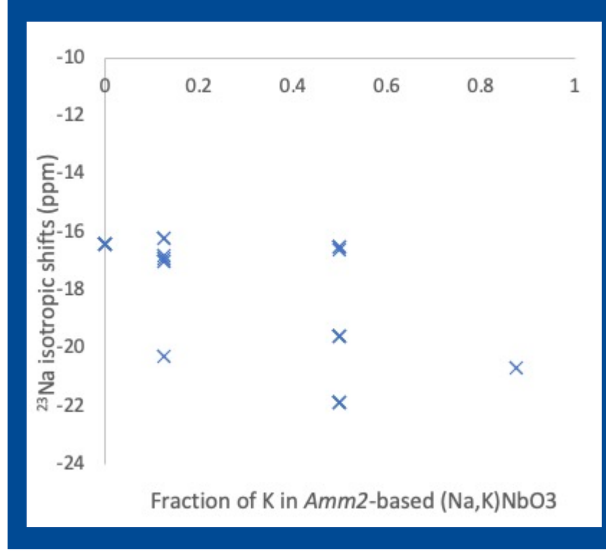
An immediate relationship can observed between the potassium content in a solid solution structure and the resultant ^{23}Na isotropic shifts for all three data sets. The more potassium is present, the lower the isotropic shifts are likely to be. This trend is very strong in the *Pbcm*- and *P2₁ma*-based sets but can be observed in the *Amm2*-based results too.

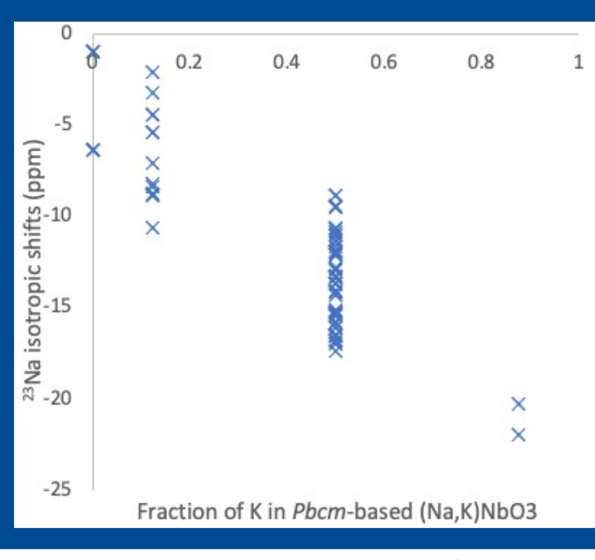
For the ^{17}O NMR results, δ_{iso} and C_Q were plotted for the range of substitutions – each structure giving a loosely linear plot, which were slightly right-shifted as the proportion of K present increased. This suggests that while K atoms shield Na atoms, they deshield O atoms, relative to Na atoms.

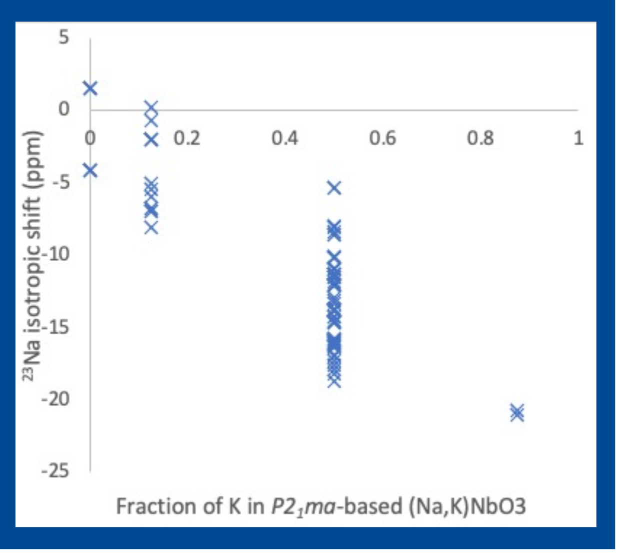


The above figure shows the relationship between δ_{iso} and C_Q over the range of substitutions for ^{17}O NMR, in the *Pbcm*-based structures. A trend can be seen between the isotropic shift and the fraction of K in the solid solution.

The below figures show the relationship between the ^{23}Na isotropic shifts and the fraction of K in the $K_xNa_{1-x}NbO_3$ structures for each set of results based on the three polymorphs.







Conclusion

A range of $K_xNa_{1-x}NbO_3$ solid solutions were successfully simulated using *Pbcm* and *P2₁ma* polymorphs of $NaNbO_3$ and $KNbO_3$ as the initial end members. The DFT functionals of PBE and PBEsol were compared for the purpose of optimisation and predicting NMR parameters of the solid solutions, and PBE was chosen for the later analysis. The relative mixing energies were positive for all three data sets - the formation of mixed-metal niobate structures is slightly disfavoured relative to these end members. The NaO bond lengths were compared to the K content of the solid solutions and referred to the bond length predicted by ionic radii. The ^{23}Na and ^{17}O NMR parameters were gathered and the relationship between increasing K fraction in the solid solution was linked to a decrease in isotropic shift for ^{23}Na.

Future Work

Further computational research can be done using slightly different solid solution compositions (*i.e.* using larger supercells to achieve finer increments of substitutions), or to investigate $LiNbO_3$, and its related solid solutions, which has also been found to be of interest in electronic applications.[14] Experimental work could also be done in synthesising structures of promise and comparing the results to those found here.

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