Investigating disorder in $A_2B_2O_7$ ceramics for waste encapsulation using NMR crystallography

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NMR spectroscopy provides an element-specific, sensitive probe of the local environment, enabling detailed information to be extracted. However, in the solid state the vast majority of this information remains unexploited, owing to the challenges associated with obtaining high-resolution spectra and the ease with which these can be interpreted. Recent advances enabling accurate and efficient calculation of NMR parameters in periodic systems have revolutionized the application of such approaches in solid-state NMR spectroscopy, particularly among experimentalists. As NMR is sensitive to the atomic-scale environment, it provides a potentially useful tool for studying disordered materials, and the combination of experiment with first-principles calculations offers a particularly attractive approach. There are, however, significant experimental and computational challenges in the application of NMR spectroscopy to disordered materials. For example, there is no longer a single arrangement of atoms in a simple model structure that matches the material under study, and many different atomic arrangements may be required to gain insight into the interpretation and assignment of NMR spectra, and ultimately, into the structure of the material under study.

The crystal chemical flexibility of pyrochlore-based ($A_2B_2O_7$) oxide materials has resulted in a wide range of applications, including energy materials, nuclear waste encapsulation and catalysis. There is, therefore, considerable interest in understanding the structure–property relationships in these materials, *i.e.*, investigating how cation/anion disorder and local structure vary with composition. Here we combine a range of ^{89}Y, ^{119}Sn and ^{17}O NMR experiments with periodic planewave calculations to explore cation disorder in ^{17}O-enriched $(Y,La)_2(Sn,Ti,Zr,Hf)_2O_7$ phases. We show how a variety of NMR crystallographic approaches from cluster-based approaches to ensemble-based modelling and the use of grand canonical ensembles can provide insight into the atomic-scale structure and disorder in these materials.[1-6]

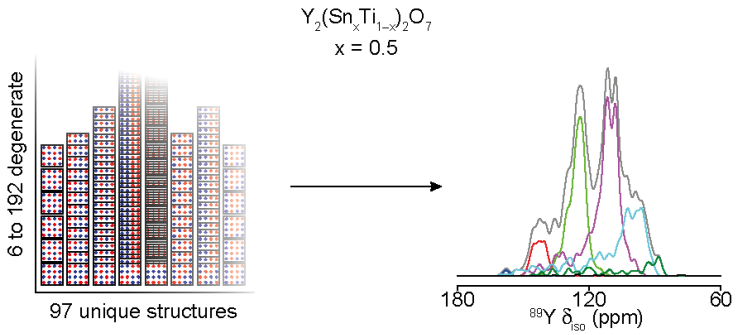

Figure 1. Ensemble-based methods for predicting NMR spectra of disordered materials

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