

**1. Title of Case Study:** High-Field Solid-State NMR for the Study of Optoelectronic Materials

**2. Grant Reference Number:** EPSRC EP/M028186/1, EP/K024418/1, EP/T015063/1, EP/R029946/1

**3. One sentence summary:** Multinuclear high-field solid-state NMR provides insight into the local structure and disorder of materials for optoelectronic applications.

**One paragraph summary:** Optoelectronic materials are important for the development of devices that transmit, convert or emit light energy with increased efficiency. In many cases, they feature highly complex structures or display intrinsic disorder or dynamics. Diffraction and electronic measurements can provide insight into the long-range structure and transport properties, and solid-state NMR can complement this by providing detailed information on local structure, dopants and substituents, which are often critical to the material properties. This case study highlights the advantages of high-field solid-state NMR for such studies and the detailed structural information that can be obtained.

**5. Key outputs in bullet points:**

- *Atomic-level structural insight into complex optoelectronic materials*
- *International research collaborations supported by the NRF*
- *Complementarity of high-field NMR with other advanced characterisation techniques*
- *Observation of challenging nuclei and thin film samples*

**6. Main body text:** Optoelectronic materials are an important class of materials with applications including photovoltaics, low energy light emission and sensing. One class of materials that have received intense interest over the last 10 years is hybrid perovskites, which show extremely high solar cell efficiencies exceeding 25%. The perovskite structure is based on organic cations within a metal halide framework. In addition to the intrinsically high charge carrier diffusion lengths, the multi-component hybrid structure offers high chemical versatility, allowing the band gap to be tuned towards particular applications. Despite the intense interest in these materials and the rapid development into what is now a mature research field, many aspects of the structure-property relationships remain poorly understood. One challenge in mixed composition hybrid perovskites is the presence of intrinsic and light-induced phase segregation which can be detrimental to the efficiency and stability. Recently, it has been found that doping a caesium cation sublattice with rubidium can suppress phase segregation in mixed halide perovskites. Wang *et al.* used  $^{133}\text{Cs}$  and  $^{87}\text{Rb}$  MAS NMR measurements at 20 T to study the cation speciation within these materials. The increased chemical shift resolution at high field made it possible to identify distinct Cs environments in single halide end members, whereas broadened lineshapes in a mixed halide I/Br compositions confirmed that all Cs was incorporated within the same phase. Viewing the same materials from the perspective of  $^{87}\text{Rb}$  NMR also confirmed that Rb cation dopants up to the studied level of 10% were fully incorporated into the Cs sublattice, supporting that the incorporation of lattice strain helps to suppress phase segregation.

Another strategy for increasing the stability of hybrid perovskites is to incorporate bulky cations to form two-dimensional structures. However, due to reduced electron mobility, these 2D structures must be aligned to maximise efficiency. Lehner *et al.* used  $^{13}\text{C}$  MAS and CPMAS NMR at 20 T as part of a study of preferential alignment in ultrathin perovskite films containing 3-fluorobenzylammonium (3FBA) cations. Here, the high magnetic field was essential to maximise the sensitivity of the dilute  $^{13}\text{C}$  nucleus within the small sample volumes studied. The increased chemical shift resolution also helped to identify subtle differences in aromatic region, indicating that the conformation of 3FBA adapts depending on the number of surrounding 3D slabs in the structure. In a separate study, Lekina *et al.* used  $^1\text{H}$  MAS NMR at 23.5 T to characterise the

dynamics of bulky hexadecylammonium (HDA) cations within a lead iodide perovskite lattice. Exploiting the increased resolution under fast MAS conditions at this magnetic field, it was possible to individually measure  $^1\text{H}$   $T_1$  relaxation constants for protons at different positions along the HDA alkyl chain. The relaxation times exhibited substantial variation whereby  $T_1$  increased with increasing distance from the  $\text{NH}_3^+$  head group. This indicates that aliphatic protons close to the  $\text{NH}_3^+$  are more mobile and dynamic than the more rigid hydrophobic portion of the HDA chain.

Vashishtha *et al.* used  $^{39}\text{K}$  MAS NMR at 20 T to provide insight into the local structure in a series of K-substituted  $\text{Cs}_2\text{AgInCl}_6$  double perovskite nanocrystals. Owing to its low gyromagnetic ratio,  $^{39}\text{K}$  is extremely challenging to observe, particularly in the presence of broadening due to disorder. By maximising the sensitivity at high magnetic field, it was possible to obtain  $^{39}\text{K}$  MAS NMR spectra in the presence of extensive structural disorder, allowing distinct environments for  $\text{K}^+$  substituted onto A and B sites within the perovskite structure to be identified and correlated with DFT-calculated chemical ranges. An important observation from this work is the pronounced changes in proportions of the different local environments as the K substitution level is varied, whereby the specific composition of 60% K provides an optimal balance between covalent character, restricted  $\text{Cs}^+$  mobility and  $\text{K}^+$  incorporation into the perovskite structure.

Another class of materials that display promising optical properties are tellurite glasses. These materials exhibit higher refractive indices, lower phonon energies, and increased infrared (IR) transmittance than silica glasses, making them promising candidates for optical applications in the near- and mid-IR. Network modifiers such as alumina are often used to increase the thermal stability and durability of tellurite glasses; however, the interdependence of glass composition, structure, and functional properties is not fully understood. Barney *et al.* used  $^{27}\text{Al}$  MAS NMR at 20 T to probe the local Al environments in a series of series of  $\text{Al}_2\text{O}_3$ - $\text{TeO}_2$  glasses with compositions up to 16 mol%  $\text{Al}_2\text{O}_3$ . The spectra enabled observation and quantification of distinct  $\text{AlO}_4$ ,  $\text{AlO}_5$  and  $\text{AlO}_6$  environments in the structure, with the high magnetic field critical for the observation of  $\text{AlO}_5$  environments which typically exhibit large quadrupolar interactions owing to the less symmetric bonding environment. The increased sensitivity and reduction of  $^{27}\text{Al}$  quadrupolar interactions at high field also enabled a  $^{27}\text{Al}$  double-quantum (DQ) dipolar correlation spectrum to be obtained, which provides direct insight into relative Al – Al proximities in the structure. This revealed a strong clustering of like pairs of  $\text{AlO}_6$  and  $\text{AlO}_4$  but not  $\text{AlO}_5$ , despite the clear presence of these in the one-dimensional spectrum. Modelling the DQ build up with spin simulations enabled a quantitative model for  $\text{AlO}_n$  distances in the structure to be obtained.

Wang *et al.*, *Nature* 2023, 618, 74; Lehner *et al.*, *Adv. Mater.* 2022, 35, 2208061; Lekina *et al.*, *J. Phys. Chem. C* 2023, 127, 33; Vashishtha *et al.*, *J. Mater. Chem. A* 2022, 10, 3562; Barney *et al.* *J. Phys. Chem. C* 2020, 124, 37.

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