Quadrupolar NMR Studies of Structure: ^{27}Al MQMAS NMR of Al_xO_y Films & ^{25}Mg MAS NMR at 35.2T SCH Magnetic Field

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Introduction

Quadrupolar species such as ^{27}Al and ^{25}Mg (both nuclear spin I=5/2) benefit from high-field NMR studies, owing to the reduction of second-order quadrupolar coupling effects as the field strength increases. We report on two studies here. First, aluminum oxide possesses a number of important properties that make it a critical component in microelectronics, protective coatings, and catalysis applications. Amorphous aluminum oxide thin films are preferred to avoid current leakage through crystalline grain boundaries. However, the lack of long-range order in amorphous samples makes the study of structure-property relationships challenging. In this project, solid-state NMR is applied to study the structure of amorphous aluminum oxide thin films. Second, the magnesium-bearing carbonate species, nesquehonite, is an important step on the pathway to CO_2 mineralization. Given the well-known crystal structure for this species, there is an opportunity to characterize its electric field gradient (EFG) tensor through 35.2T studies.

Experimental

Aluminum oxide thin films were prepared by well-established routes [1]. The two-dimensional 3QMAS experiments of a 500 °C film were conducted at 19.6T, with a 3.2 mm probe, with a MAS frequency of 18 kHz. The excitation and reconversion pulse lengths 3.7 μs and 1.3 μs were used with a z-filter 3QMAS sequence. Nesquehonite samples were acquired. ^{25}Mg NMR was acquired using the “Bloch decay” sequence (non-quantitative) with a π/2pulse length of 10 μs at 35.2T, with a 3.2 mm probe, at a MAS frequency was 10 kHz.

Results and Discussion

Fig. 1 shows ^{27}Al 3QMAS NMR of Al_xO_y film annealed at 500 °C. At this field, the n-coordinate Al-O polyhedral sites, $^{[4]}$Al, $^{[5]}$Al and $^{[6]}$Al, are reasonably resolved, which is shown as three contours in the 3QMAS NMR from left to right. $^{[n]}$Al represents the coordination number of the aluminum sites. This 2-dimensional spectrum enables both resolution of the different sites present, and extraction of the quadrupolar coupling parameter, used for deconvolution of 1-dimensional spectra (for quantitation). Quantitatively determining the $^{[n]}$Al sites ratio in AlxOy films requires knowledge of quadrupolar parameters. In work being prepared for publication now, the structural changes for films at different annealing temperatures can be monitored. (Draft paper, in preparation).

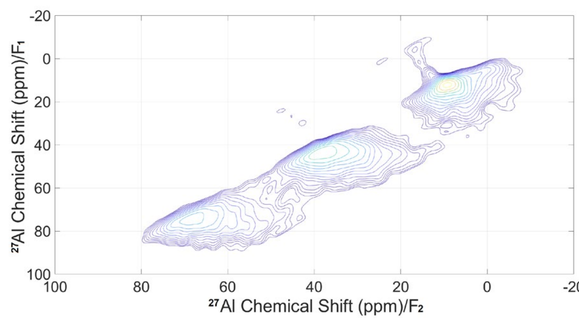

Fig. 1 3QMAS ^{27}Al NMR of AlxOy film annealed at 500 °C. [2]

Fig. 2 exhibits ^{25}Mg solid-state MAS NMR of a single magnesium site present in the mineral, nesquehonite, $Mg(HCO_3)(OH)\cdot 2(H_2O)$ at 35.2T. Computational modeling of the EFG tensor is being pursued currently, to compare atomic coordinates with the experimentally-measured ^{25}Mg solid-state NMR data.

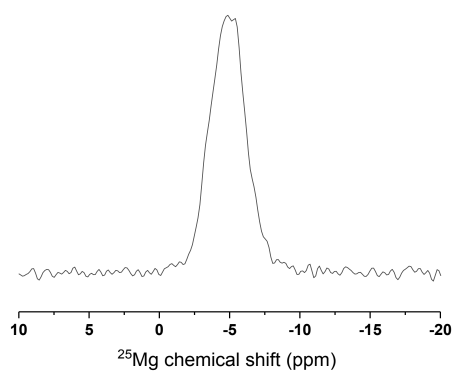

Fig. 2 ^{25}Mg NMR of nesquehonite

Conclusions

Quadrupolar NMR requires high and ultra-high fields to help untangle complicated spectra. Here, ^{27}Al resonances could be assigned and deconvoluted based on high-field 3QMAS results, which will influence multiple studies of aluminum oxide high-k dielectric thin films. In addition, ^{25}Mg solid-state NMR offers the first opportunity to examine this low-γ (gyromagnetic ratio) species for which there are few studies. Having the EFG tensor for this species can enable a range of future ^{25}Mg studies in different coordination environments, beyond carbonates.

Acknowledgements

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References

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[2] Cui, J.L., *et al*., Chemistry of Materials, **30**, 7456-7463 (2018).