SSNMR Spectroscopy of Methylammonium Tin Halides

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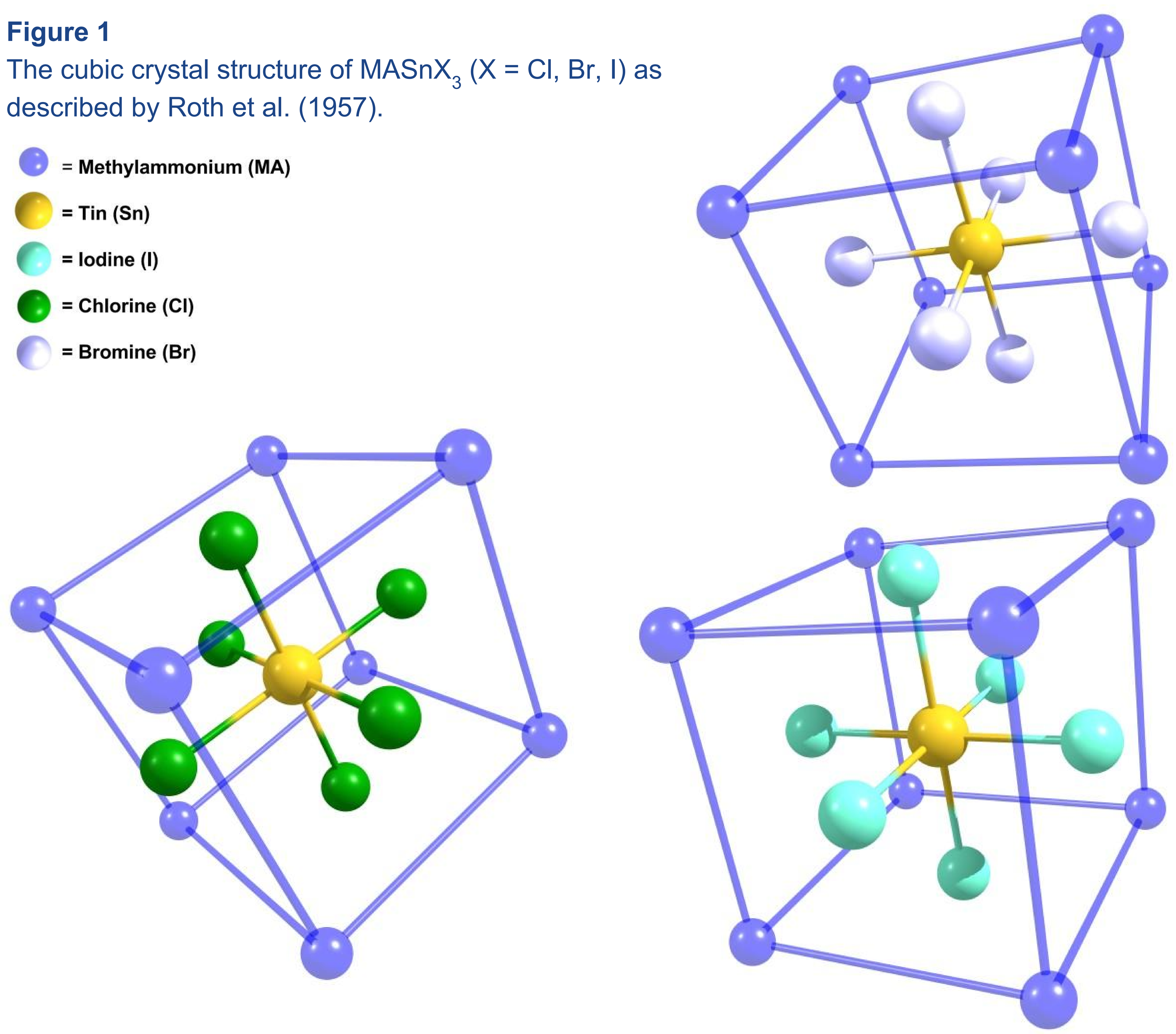
Introduction:

- Solid-state nuclear magnetic resonance (SSNMR) spectroscopy uses the magnetic properties of nuclei to gain information on molecules.[1]
- As the demand for energy increases around the globe, research focusing on sustainable energy sources, such as solar cell technologies, is key.
- Perovskites may be used to gather light as hole-transport materials in solar cells [2] and are beginning to emerge in solar cell technologies due to several qualities that allow them to achieve high power conversion efficiencies (PCEs).[3]
  - Small exciton binding energy
  - Ambipolar charge mobility
  - Strong light absorption
  - Tolerance to defects
- In solar cells, methylammonium lead halide ($MAPbX_3$) perovskites have the highest PCEs [1] but as lead is harmful to the environment, alternate perovskites (such as methylammonium tin halides ($MASnX_3$)) are of interest.[4]
  - Atmospheric instability of tin reduces the lifespan of lead-free $MASnX_3$ cells significantly.[2]
- Perovskites are crystalline solids that are described by the formula ABX_3 [2]

Figure 1
The cubic crystal structure of $MASnX_3$ (X = Cl, Br, I) as described by Roth et al. (1957).



Purpose:

- To determine the unique ^{119}Sn SSNMR spectra of the $MASnX_3$ (X = Cl, Br, I).

Methods:

- Using a Bruker Avance 7.05 T spectrometer with resonance probe, we analysed the ^{119}Sn NMR of a series of $MASnX_3$ perovskites.
- The reference sample for ^{119}Sn NMR was tetracyclohexyltin (-97.35 ppm).
- Non-spinning and magic-angle spinning (MAS) experiments at 8, 10 and 12 kHz were acquired using a Hahn-echo pulse program.
- $MASnCl_3$ delay = 60 seconds
- $MASnBr_3$ delay = 45 seconds

Figure 2
A rotor that would contain a sample to be inserted into the SSNMR spectrometer.

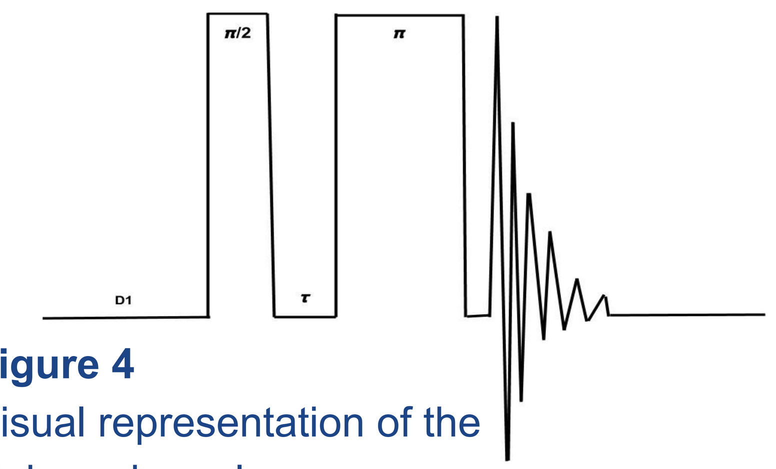


Figure 4
Visual representation of the Hahn-echo pulse program.

Figure 3
Bruker Avance 7.05 T spectrometer used to gather the spectra.

Results:

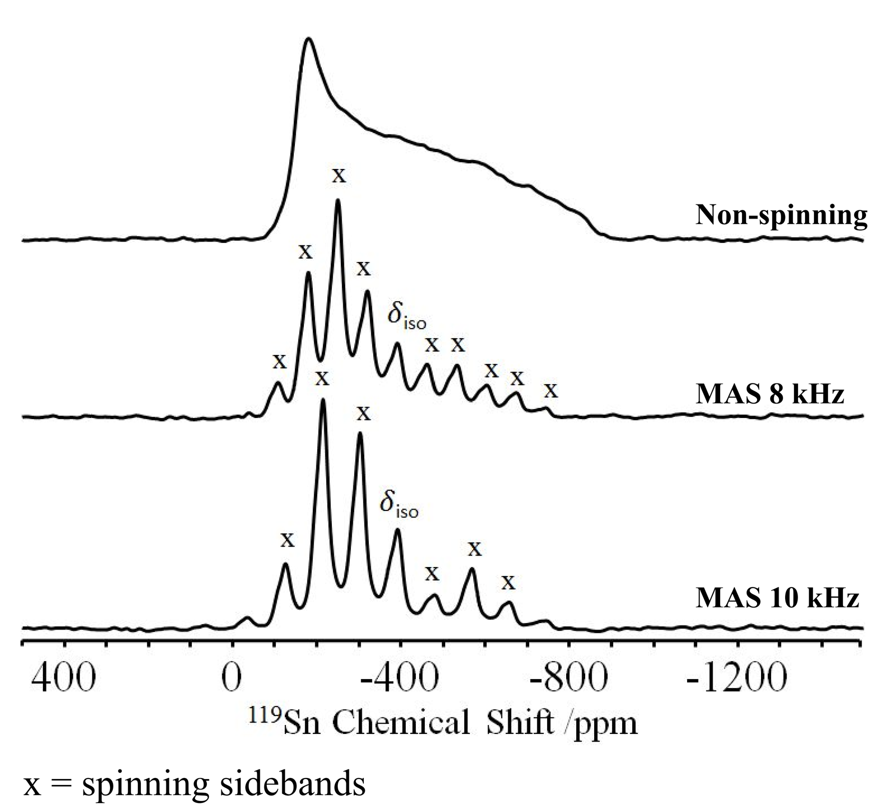


Figure 5
^{119}Sn NMR of $MASnCl_3$ δ_{iso} = -392 ppm.

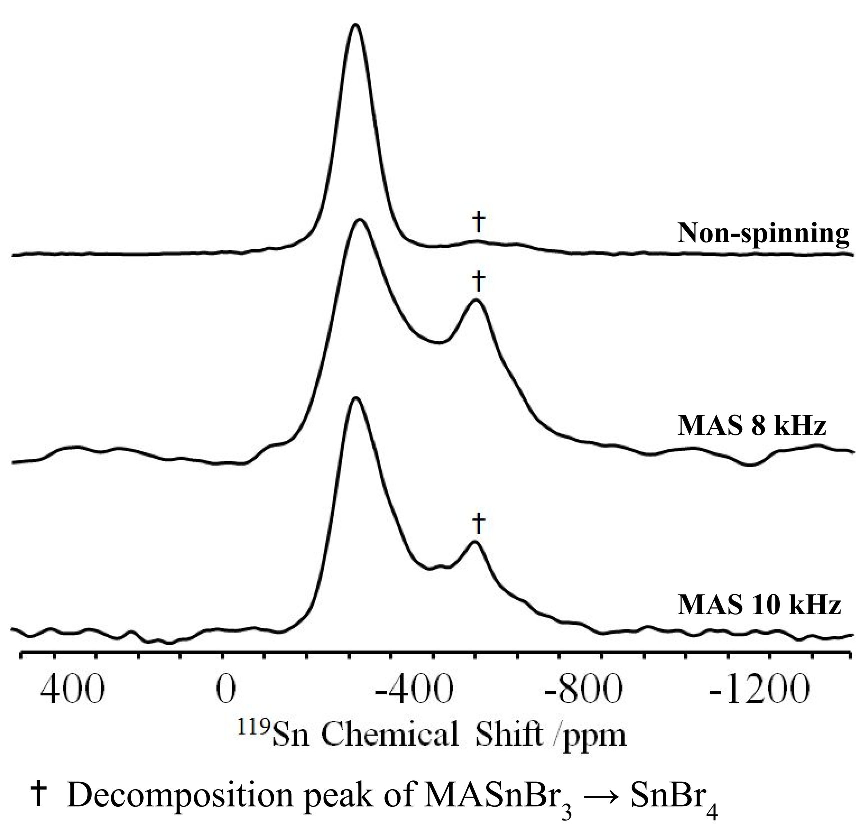


Figure 6
^{119}Sn NMR of $MASnBr_3$ δ_{iso} = -322 ppm.
δ_{iso} of $SnBr_4$ = -601 ppm.[6]

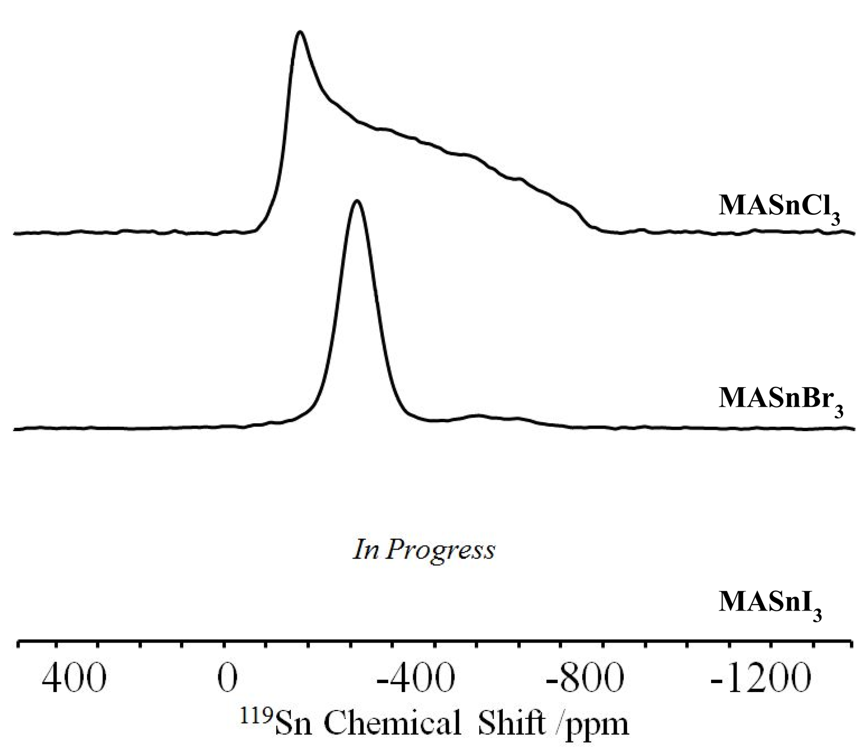


Figure 7
Comparison of ^{119}Sn NMR of $MASnX_3$ non-spinning spectra.

Conclusions:

- $MASnCl_3$ and $MASnBr_3$ have varying peak widths with chemical shifts that increase from the chlorine to the bromine samples.
- The bromine sample appears to have a broad peak both in the non-spinning and MAS spectra.
- The $MASnI_3$ spectra will be completed in order to finish this experiment.
- Future work may consider the effect of different synthetic techniques used to create $MASnI_3$ samples on stability.
  - The relation of the phases of the different samples may also be examined in relation to stability.

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