Application of Nuclear Magnetic Resonance to the Study of Nuclear Waste Relevant Molybdates at Ambient and High Temperatures

by

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“I may not have gone where I intended to go, but I think I have ended up where I needed to be.”

Douglas Adams
Abstract

High-Level Waste (HLW), contains radioactive isotopes with half-lives upwards of millions of years. The long-term storage of HLW can be accomplished through vitrification of the mixture in a borosilicate melt, producing a chemically inert solid. Unfortunately, molybdates can precipitate from the glass melt as water-soluble oxides containing radionuclei. Part of this study is dedicated to the characterization and interpretation of the NMR parameters for a series of crystalline molybdate phases at ambient temperatures. $^{23}$Na, $^{95}$Mo and $^{133}$Cs MAS NMR data were correlated to the local structure and geometry, showing several key trends. From the ambient temperature studies, select crystalline phases were chosen for high-temperature experiments up to 700°C. These experiments were used to characterize the behaviour of these phases at temperatures relevant to both the formation of solid waste forms and their long-term storage. With these spectral “fingerprints”, it is possible to monitor the phase separation behaviour at temperatures relevant to vitrification and long-term geological storage. For example, the conversion of CsNaMoO$_4$·2H$_2$O into Cs$_3$Na(MoO$_4$)$_2$ and Na$_2$MoO$_4$ can be followed in situ through MAS NMR. Finally, a series of model nuclear waste glasses with varying amounts of Cs and Mo were studied, allowing direct observation of the crystallization process.
Acknowledgements

This thesis could not have been accomplished without the support of my supervisor, colleagues, friends and family. Firstly, I recognize the immense contribution of my supervisor, Dr. Scott Kroeker, has made to this work. It is only through his guidance and keen attention to detail that the ideas within this thesis could be brought to fruition. Rhys Sharkey is acknowledged for his role assisting me during the initial stages of this project. I would also like to thank Dr. Vladimir K. Michaelis, who taught me the basics of experimental NMR, as well how to look at every problem with the question, “What’s the spin of that nucleus?” I thank Mr. Brandon J. Greer and Dr. Randi Christensen for their camaraderie and aid throughout the years. I appreciate the efforts of our many former undergraduate students: Heather Cavers, Kimberley Craigen, Stan Giesbrecht, Carolyn Higman, Palak Kachhadia, Kirill Levin, Lawson Miller, Alex Paterson, David Snider and Connor Zeer-Wanklyn. It is my pleasure to recognize the support and influence of my committee members on the creation of this document: Dr. Barbara Sherriff (Dept. of Geological Sciences), Dr. Sean McKenna and Dr. Georg Schreckenbach (Dept. of Chemistry). I would like to express gratitude to: Dr. Kirk Marat, whose NMR expertise is second-to-few and Dr. Mario Bieringer and his group, who have always been generous with their XRD experimentation and speciality. I would not be here without the inspiration from my dad’s inquisitive nature or my mom’s encouragement to never stop achieving. Finally, I dedicate this work to my wife, Christine, whose support and understanding has been essential to my success.
For Christine
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Abbreviations

CSA  Chemical Shift Anisotropy
CT   Central Transition
DR   Double Resonance
DTA  Differential Thermal Analysis
EFG  Electric Field Gradient
FT   Fourier Transform
HLW  High Level Waste
HT   High Temperature
ICP  Inductively Coupled Plasma
LA   Laser Ablation
LT   Low Temperature
MAS  Magic Angle Spinning
MS   Mass Spectroscopy
NMR  Nuclear Magnetic Resonance
ppm  parts per million
SNF  Spent Nuclear Fuel
ssb  spinning side band
ST   Satellite Transition
TGA  Termogravimetric Analysis
XRD  X-Ray Diffraction
### Physical Constants

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<td>Speed of Light in a vacuum</td>
<td>$c = 2.997 924 58 \times 10^8 \text{ ms}^{-1}$ (exact)</td>
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<tr>
<td>Boltzmann Constant</td>
<td>$k = 1.380 648 8(13) \times 10^{-23} \text{ J K}^{-1}$</td>
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<td>Planck’s constant</td>
<td>$h = 6.626 068 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$</td>
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<td>$e = 1.602 176 565 \times 10^{-19} \text{ C}$</td>
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<tr>
<td>Avogadro’s number</td>
<td>$N_A = 6.022 141 5 \times 10^{23}$</td>
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<tr>
<td>Magnetic Constant</td>
<td>$\mu_0 = 5\pi \times 10^{-7} \text{ H m}^{-1}$</td>
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## Symbols

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<th>Description</th>
<th>Units / Definition</th>
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<td>Angular Frequency</td>
<td>rad ( s^{-1} )</td>
</tr>
<tr>
<td>( T_f )</td>
<td>Fictive Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>( T_g )</td>
<td>Glass Transition Temperature</td>
<td>°C</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Gyromagnetic Ratio</td>
<td>rad ( s^{-1} ) T(^{-1} )</td>
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<tr>
<td>( \delta_{iso} )</td>
<td>Isotropic Shift</td>
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<tr>
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<td>Larmor Frequency</td>
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<tr>
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<td>Quadrupole Moment</td>
<td>mb</td>
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<tr>
<td>( C_Q )</td>
<td>Quadrupole Coupling Constant</td>
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<td>( \Omega )</td>
<td>Span</td>
<td>( \delta_{11} - \delta_{33} ); (( \Omega \geq 0 ))</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Skew</td>
<td>( \frac{3(\delta_{22} - \delta_{iso})}{\Omega} ); (( -1 \leq \kappa \leq 1 ))</td>
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Chapter 1

Introduction

1.1 Nuclear Industry

Nuclear power currently accounts for 12.9% of the world’s domestic electricity generation. Countries such as France and Canada draw upwards of 75.9 and 14.9% of their electricity from nuclear power sources, respectively.[1] By 2035 projections suggest that as much as 7 to 11% of the world’s total power could be from nuclear power sources (versus 5.7% in 2010). Although current global politics disfavour the proliferation of nuclear power, commercial plants have been active since 1954 and with their operation there has been a continuous production of radioactive waste. It is estimated that globally 15,000,000 kg of waste is produced annually from nuclear power plants.[2] As of 1995, the Hanford waste storage site...
in Washington, USA, stores >11,000 $m^3$ of low- and high-level liquid waste and 6,900 tons of solid waste.[3]

1.1.1 Production of Nuclear Power and Waste

Nuclear power is superficially a simple concept but with a rather wide variation in implementation from country to country and reactor to reactor. The nuclear fuel cycle (Figure 1.1) begins with the mining and milling of raw uranium minerals into U$_3$O$_8$, also known as “yellow cake”. This fuel precursor typically has a $^{235}$U content of $\leq 0.7\%$, which is considered insufficient for most reactor designs. Yellow cake is either directly converted to the active fuel material, UO$_2$, or to gaseous uranium hexafluoride, UF$_6$. The gaseous UF$_6$ is split into two streams using a centrifuge based process to produce both $^{235}$U enriched (3.5 - 5%) and depleted uranium ($^{238}$U) sources. The enriched $^{235}$U UF$_6$ is converted to UO$_2$ which is sintered into ceramic fuel pellets, of which the design, size and composition are highly controlled and relatively unique to a given reactor.[2, 4]

Within the reactor, the $^{235}$U in the fuel assembly undergoes a fission process upon neutron bombardment. This reaction splits the nucleus into various daughter products, releasing large amounts of energy. The heat emitted from the fuel is used to produce steam which in turn drives a turbine generator, converting the thermal energy into electricity.
Figure 1.1: Schematic of the nuclear fuel cycle employed in countries that reprocess their spent nuclear fuel.

This process depends on the continuous chain reaction of fission events, the efficiency of which is related to the distance between $^{235}$U isotopes. The decay in efficiency with fuel consumption requires that approximately every 18 months one
third of the fuel assemblies must be replaced in a given reactor, i.e. an effective lifespan of 54 months for each rod.

1.1.2 Nuclear Waste

Spent nuclear fuel (SNF) removed from the reactors still has unreacted $^{235}\text{U}$, upwards of 95% of the original enrichment.\textsuperscript{[2, 4]} Many countries, notably France and Japan, have reprocessing programs where the SNF is dissolved in acids and the $^{235}\text{U}$ is separated for incorporation in new fuel rods. Unfortunately this process produces large quantities of liquid HLW, containing a diverse set of radioactive daughter isotopes, table \ref{tab:daughter-products}.

<table>
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<th>Radionuclide</th>
<th>Half life (years)</th>
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<td>$^{90}\text{Sr}$</td>
<td>28.8</td>
<td>$\beta$</td>
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<td>$^{93}\text{Zr}$</td>
<td>$1.53 \times 10^6$</td>
<td>$\beta, \gamma$</td>
</tr>
<tr>
<td>$^{99}\text{Tc}$</td>
<td>$2.1 \times 10^5$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>$^{129}\text{I}$</td>
<td>$1.6 \times 10^7$</td>
<td>$\beta, \gamma$</td>
</tr>
<tr>
<td>$^{133}\text{Cs}$</td>
<td>$2.3 \times 10^6$</td>
<td>$\beta$</td>
</tr>
<tr>
<td>$^{137}\text{Cs}$</td>
<td>30.17</td>
<td>$\beta, \gamma$</td>
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Nuclear waste has accumulated over the past 60+ years, from both weapons production and nuclear power sources. The requirement for a sustainable long-term storage solution for this HLW has driven a branch of materials research for nearly as long as the waste has been produced.\textsuperscript{[3–7]} Arguably the most important aspect of radioactive waste storage is the immobilization and segregation of these elements from the environment. The contamination of ground water sources would
be particularly devastating, as it would allow for rapid distribution of the waste to the nearby environment. The materials used to store these wastes must be capable of retaining a very wide variety of elements (≥ 20), their various isotopes and their daughter products, over the course of many thousands of years. These materials must be durable for upwards of 10,000 years or longer to reach “safe” radiation levels (0.1% of their initial radioactivity).[2] The current USA governmental policies demand a sustainable storage solution be chemically inert for one million years or longer.[8]

The current method for immobilizing liquid HLW (Figure 1.2) involves dissolving the waste in a borosilicate glass matrix to form a vitreous solid. Crystalline materials have also been shown to be effective for the storage of certain isotopes, but there are concerns over long-term structural stability. It was found that the recoil from α decay processes of actinides held within crystalline zircon (ZrSiO$_4$) was highly destructive.[9] It was predicted from these studies that at 10 wt. % $^{239}\text{Pu}$, a zircon based storage material would be completely amorphous after only 1,400 years, a fraction of the expected storage time. By using a disordered solid, the effect of these decay processes on structure is minimal, endowing it with superior longevity.

These waste materials must also be thermodynamically stable at relatively elevated temperatures due to the radioactive emissions. The heat produced by decay within these materials could result in initial glass temperatures as high as 800°C.[10] The
actual temperature of the glass will depend on the glass composition and storage site, specifically the cooling methods employed. Current storage site designs expect to reduce the surface temperature of these glasses to \( \leq 200^\circ C \) and the centreline temperature to \( \leq 400^\circ C \). As the large portion of its radioactive life will be spent at elevated temperatures, the study of model nuclear waste systems must be adapted to account for these thermal effects.

1.1.3 Production of Vitreous Waste Forms

The process for production of solid vitreous waste forms (figure 1.2) begins with the calcination of the liquid HLW at 1000-1200\(^\circ\)C, driving off the water and nitrates, leaving a radioactive powder. This calcine is then added to a molten borosilicate glass precursor, also known as the glass frit, at 1000-1200\(^\circ\)C. The temperature must be kept below 1300\(^\circ\)C, due to the volatility of cesium above these temperatures. The mixture is finally poured into a storage canister and rapidly cooled, typically at rates around 1\(^\circ\)/minute. The glass precursor has a general formula of approximately 40-55 wt. % \( \text{SiO}_2 \), 5-15 wt. % \( \text{B}_2\text{O}_3 \) and 8-20 wt. % \( \text{Na}_2\text{O} \), although the development and optimization of this composition is in itself a large area of research. The composition of the glass is important in dictating the “loading” of HLW that can be safely dissolved without inducing phase separation upon cooling. Current theoretical loadings are in the range of 25-35 wt. % HLW, although some
Figure 1.2: Schematic of the production of vitreous waste forms.
novel glass compositions have shown the capacity for as much as \( \leq 50 \) wt. \%, table 1.2.[4, 11]

**Table 1.2: Examples of nuclear waste glass compositions**

<table>
<thead>
<tr>
<th>Glass, Country</th>
<th>SiO(_2) (wt. %)</th>
<th>B(_2)O(_3) (wt. %)</th>
<th>Al(_2)O(_3) (wt. %)</th>
<th>CaO (wt. %)</th>
<th>MgO (wt. %)</th>
<th>Na(_2)O (wt. %)</th>
<th>Misc (wt. %)</th>
<th>Waste loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>R7/T7, France</td>
<td>47.2</td>
<td>14.9</td>
<td>4.4</td>
<td>4.1</td>
<td>–</td>
<td>10.6</td>
<td>18.8</td>
<td>( \leq 28 )</td>
</tr>
<tr>
<td>DWPF, USA</td>
<td>49.8</td>
<td>8.0</td>
<td>4.0</td>
<td>1.0</td>
<td>1.4</td>
<td>8.7</td>
<td>27.1</td>
<td>( \leq 33 )</td>
</tr>
<tr>
<td>Magnox Waste, UK</td>
<td>47.2</td>
<td>16.9</td>
<td>4.8</td>
<td>–</td>
<td>5.3</td>
<td>8.4</td>
<td>17.4</td>
<td>( \leq 25 )</td>
</tr>
<tr>
<td>LILW K26, Russia</td>
<td>43</td>
<td>6.6</td>
<td>3.0</td>
<td>13.7</td>
<td>–</td>
<td>23.9</td>
<td>9.8</td>
<td>35</td>
</tr>
</tbody>
</table>

### 1.2 Vitreous Materials

Glasses are formed by rapidly cooling a liquid to a point below the melting temperature \( (T_m) \), thereby reaching a local minimum before the atoms can rearrange into a crystalline arrangement.[12, 13] Crystalline solids are ordered arrangements of atoms, displaying periodic translational order along their three axes.[14] The transition from a liquid to a crystal is a time-dependent process, requiring time for the free moving atoms in the liquid to arrange in the given crystalline arrangement upon cooling. Cooling a liquid increases its viscosity, decreasing the mobility of its atoms. Provided the cooling is rapid, it is possible to increase the viscosity
Figure 1.3: Representation of the effect of temperature on the enthalpy of a glass-forming melt. The glass formation temperature, $T_g$, lies within the glass formation region.

faster than the atoms can rearrange, producing a kinetically arrested solid. Vitreous materials do not display any long-range order beyond the first or second coordination sphere. The structure and properties of a glass are strongly dependent on the arrangement of short-range order (SRO) structural units. These SRO units are the first coordination sphere arrangement of the glass-forming cations and adjoining anions. SRO units can take a multitude of forms including, but not limited to, pseudo-trigonal planar and pseudo-tetrahedral units. The arrangement
of SRO units within the glass is dependent on the cooling rate used to solidify the material. The fictive temperature, $T_f$, is the point at which the extrapolated slopes in enthalpy for the glass and supercooled liquid intersect, and is often used to give some measure of the thermal history of the glass (Figure 1.3). Although the transformation of the melt into a solid occurs over a range of temperatures a glass-formation temperature, $T_g$, is commonly defined for a given composition. This value is derived from either thermal analysis or thermal expansion curves, with the determined value differing based on the method. Although the value for $T_g$ is often somewhat arbitrary, it can still be used as an indicator of the approximate temperature where the supercooled liquid converts to a solid on cooling, or vice versa.\textsuperscript{[13]}

Nuclear waste glasses are formed from the cooling of a liquid mixture of various oxides. In oxide glasses, the structure is formed by a network of cations held together by a combination of ionic and covalent bonds to oxygen. The cations used in the formation of these glasses fall into one of three categories: glass formers, modifiers, or intermediate formers. The category of SRO unit a cation will form is dependent largely on the “field strength” of the ion. This is a measure of the charge ($Z$) of the ion divided by the interatomic distance between the cation and its adjacent anion, $(d(M-O))$, thereby indicating the charge concentration of the cation (Equation 1.1).\textsuperscript{[13]}

$$\text{Field Strength} = \frac{Z}{d(M-O)^2}$$  \hspace{1cm} (1.1)
A high cation field strength implies a concentrated charge, typically resulting in smaller coordination numbers and stronger bonding, while a low field-strength implies more ionic character to the bonding and larger coordination spheres.

Glass formers (e.g., B, P, Si) are cations which have a moderate to high cation field strength ($\approx 1.5...2.0$), allowing for the formation of covalent bonds to the anions (Table 1.3). Modifiers (e.g., Li, Na, Ca) are low cation field strength ions ($\approx 0.1...0.4$), resulting in weak ionic bonds. Intermediate glass formers (e.g., Al, Ga, Ti) typically have a moderate to low cation strength ($\approx 0.5...1.0$) resulting in the ability to form either ionic or covalent bonds. Glass formers form the majority of the network through the interconnection of SRO units, while modifiers interrupt the network with the creation of ionic bonds. Several strong glass forming ions can be used to form glasses without any modifiers, (e.g., SiO$_2$, B$_2$O$_3$, P$_2$O$_5$). These are largely the exception, with most “pure” former glasses having a high tendency to crystallize without very rapid cooling. The introduction of glass modifiers interrupt the glass network, which reduces the degree of connectivity and encourages disorder. Intermediate glass formers cannot form glasses without the presence of some modifier cations, but their addition to glass compositions often provides improvements in homogeneity and structure.[12, 13, 16, 17]

The disordered structure of glass has the benefit of being able to incorporate impurities into its matrix with minimal effects on the bulk material. This is contrary to crystalline materials, where the incorporation of additional elements into a given
Table 1.3: Field Strengths of Various Ions

<table>
<thead>
<tr>
<th>Element</th>
<th>Valence (Z)</th>
<th>Field strength in oxide glass</th>
<th>Function in Glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>[6]Na</td>
<td>1</td>
<td>0.19</td>
<td>Network</td>
</tr>
<tr>
<td>[6]Li</td>
<td>1</td>
<td>0.23</td>
<td>Modifier</td>
</tr>
<tr>
<td>[8]Ca</td>
<td>2</td>
<td>0.33</td>
<td>$\frac{Z}{d(M-O)^2} \approx 0.1...0.4$</td>
</tr>
<tr>
<td>[8]Sr</td>
<td>2</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>[4]Zr</td>
<td>4</td>
<td>0.77</td>
<td>Intermediate</td>
</tr>
<tr>
<td>[6]Al</td>
<td>3</td>
<td>0.84</td>
<td>Former</td>
</tr>
<tr>
<td>[4]Al</td>
<td>3</td>
<td>0.96</td>
<td>$\frac{Z}{d(M-O)^2} \approx 0.5...1.0$</td>
</tr>
<tr>
<td>[4]B</td>
<td>3</td>
<td>1.34</td>
<td>Network</td>
</tr>
<tr>
<td>[5]B</td>
<td>3</td>
<td>1.63</td>
<td>Former</td>
</tr>
<tr>
<td>[4]Si</td>
<td>4</td>
<td>1.57</td>
<td>$\frac{Z}{d(M-O)^2} \approx 1.5...2.0$</td>
</tr>
<tr>
<td>[5]P</td>
<td>4</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>

composition creates structural defects. Defects in a crystal disrupt its periodicity, producing complications in the chemistry, structure and other properties of the material. In glasses there is no periodicity to interrupt, therefore the effects of the dopants are not translated through the entire material.\[12\] \[13\]

1.2.1 Phase Separation

In an ideal glass the material is homogenous, being formed of a completely random arrangement of SRO units. In practice, it is found that there are both compositional and practical limitations on the ability of a glass to form a homogenous network.\[12\] \[13\] From a practical standpoint, the cooling of a glass melt is always non-instantaneous and non-homogenous across the sample, although there are techniques that reduce these effects (e.g. roller-quenching).\[12\] \[13\] Due to the dependence of the glass properties on the effective cooling rate, non-homogenous
cooling can produce differences in density and SRO structure across the material. Controlling the changes in bulk properties across the sample is a wide field of study with applications in a variety of technologies, from shatter resistant glasses to fibre optics. Unfortunately heterogeneous cooling implies a gradient in cooling rates across the material, with slow cooling rates increasing the degree of possible phase separation.

Non-instantaneous cooling can allow for the rearrangement of the elements in the melt into separated domains of different compositions. Upon further cooling these domains can form interpenetrated glasses of differing compositions. This type of glass-glass phase separation is quite common for certain borosilicate compositions, termed the “immiscibility region”. Non-ideal cooling rates can also allow for the partitioning of elements into ordered domains within the bulk disordered matrix, producing crystalline phase(s) upon further cooling. The presence of either glass-glass or glass-crystalline phase separation results in deviations in structure at the interface between the phases producing points of structural weakness. Phase separation also changes the composition of the bulk phase, and therefore its predicted properties. The incorporation of crystalline phases in the glass matrix is typically more concerning in terms of the materials’ durability, due to the larger deviation in structure and properties between the crystalline and glass phases.

Due to the large batch sizes used in the production of glassy waste forms, the cooling rate is typically no faster than 1°C/minute. This is a relatively slow cooling
rate for these glass compositions, resulting in an increased chance of phase separation, either glass-crystalline or glass-glass. The presence of heterogeneity in the material weakens it structurally and chemically, affecting its long-term durability. The possibility of phase separation is aggravated by the presence of high field strength cations such as molybdenum (VI), ($^{^{6}}\text{Mo}^{+6}$ field strength = 1.93). Molybdenum is both a daughter product in the uranium decay cycle, as well as being an additive in the nuclear fuel, which improves its efficiency. $^{[4]}$ $\text{Mo}^{6+}$ forms MoO$_{4}^{2-}$ tetrahedral units in these oxide systems, with the Mo-O bonds having partial double bond character. The strong covalent Mo-O bonds result in weak ionic bonds between the MoO$_{4}^{2-}$ unit and nearby low field strength cations (Na$^+$, Cs$^+$, Ca$^{+2}$, etc.). Since the molybdenum SRO units do not connect covalently to the other glass formers they become dissociated from the network, forming molybdenum-rich domains. These domains sequester low field strength cations from the bulk glass and upon cooling the ions become ordered, forming a variety of crystalline alkali and alkaline earth salts. The most common salts found in model nuclear waste glasses are Cs$_{3}$Na(MoO$_{4}$)$_{2}$, Na$_{2}$MoO$_{4}$, Na$_{2}$MoO$_{4}$·2H$_{2}$O and CsNaMoO$_{4}$(l).$^{[7]}$ The cesium within these salts is of particular concern, as $^{135}\text{Cs}$ is one of the longest lived radionuclides present in nuclear waste, (table $^{[1,2]}$). In addition to the structural weakness that the presence of these crystalline phases can have on the bulk material, these crystalline phases are highly water soluble. The risk of these materials containing radioactive water soluble phases would be detrimental to their global application. To date, crystallization has been limited
by using low waste loadings in the glass, thereby reducing the total molybdenum content, which decreases the probability of theses phases forming. Unfortunately by reducing the amount of waste in each storage canister, the total waste volume rapidly increases and this comes with equally large increases in costs and resources required for their storage. By understanding the chemistry that leads to the formation of these phases it should be possible to develop an alternative solution to waste loading reductions. These phases and their formation are strongly tied to the thermal history of the material, as such, any study that hopes to explore the chemistry at these early stages of nucleation requires a method that can be employed at elevated temperatures.

1.3 Challenges of Studying Nuclear Waste Storage Materials

Nuclear waste glasses are particularly challenging to study as they must incorporate a wide variety of isotopes, ($\geq 20$), in various concentrations and phases. The study of solid state materials uses a wide variety of analytical tools to achieve structural and compositional information. Common techniques include nuclear magnetic resonance (NMR), X-ray diffraction (XRD), Raman/Infrared (IR) spectroscopy, electron microprobe analysis (EMPA), inductively coupled plasma mass
spectroscopy (ICP-MS). Due to the phase separation and compositional complexity in nuclear waste materials there are few methods which are well adapted for these studies.

1.3.1 X-ray Diffraction

X-ray diffraction is the most common technique for the determination of structure in the study of crystalline phases. Structure and phase identification of pure crystalline phases is routinely accomplished by powder or single crystal diffraction. Multi-phase materials cannot be studied by single crystal diffraction, only by the less precise powder XRD. Although the solution of powder XRD patterns of mixed crystalline phases is possible, it is particularly challenging. The powder XRD diffracogram consists of a series of inflections, the position and intensities of which are dependent on the structure of the crystalline phase. The pattern of the diffracogram can either be used to predict the crystal structure or, more commonly, compared with a database of pre-established patterns for quick structure identification. In polycrystalline mixtures, the patterns for each diffracogram may be overlapped and inseparable. This can make the initial task of identifying the origins of each peak difficult, thereby limiting the likelihood of phase identification or quantification. The identification of novel phases in these materials is also challenging, since the patterns are inseparable.
The sharpness of the reflections in the powder XRD diffractogram is dependent on the degree of periodicity of the sample. Amorphous samples produce only broad and featureless reflections. These “patterns” have been applied to simple glass compositions to determine domain sizes, but are of little use for complex glass systems. To date there has been limited success in characterizing these materials using XRD, although it is an ongoing field of study.

1.3.2 Analytical Solid-State Methods

There are several well developed methods for studying the composition of solid materials. Scanning electron microscope (SEM) can provide an image with nanometer resolution of the surface of the sample by bombarding the sample with an electron beam and interpreting the intensity of the scattered electrons. Using SEM, effective measurements of the topography of a sample surface are possible, as well as a qualitative chemical composition.

Electron microprobe analysis (EMPA) is commonly applied in tandem with SEM to provide quantitative measurements of the chemical composition of the sample. Each element has a characteristic X-ray emission spectrum upon bombardment by electrons. EMPA compares the intensity of a given X-ray emission from a sample with the intensity from a standard with a predetermined concentration of the same element, thereby determining the elemental composition of the sample. EMPA is able to determine concentrations down to 100 ppm for most elements.
measurements can be used to characterize the surface and near-surface composition for several elements at a time. There are some challenges in EMPA due to the overlapping emission wavelengths for several elements. Additionally, due to the requirement for comparison to a standard for each analysis, the elements in the sample should be known before the experiment for efficient analysis. Elements lighter than boron do not have sufficient X-ray emissions to be analyzed by EMPA, while boron and other light elements such as sodium can become mobile under electron beam bombardment, affecting the accuracy of their measurements.

Inductively coupled plasma mass spectrometry (ICP-MS) is a more sensitive technique for compositional analysis. ICP-MS is performed on a nebulized sample of liquid containing the dissolved material. Upon introduction into the plasma torch the elements of the material are ionized and separated within the mass spectrometer, identifying the elements and their concentrations. This method requires the injection of a solution of the sample into the plasma torch chamber, therefore, the method is destructive, requiring the dissolution of the sample. In the case of chemically durable materials, such as nuclear waste glasses, dissolution is typically accomplished using hydrofluoric acid, a notably dangerous solvent. Laser-Ablation (LA)-ICP-MS is an extension of ICP-MS for solid samples, which employs a laser to ablate the sample in its natural state. When the laser is made incident on the sample, the produced particulates are guided by a flow of argon gas into the plasma chamber, allowing for an ICP-MS spectrum to be collected. This addition to the ICP-MS method allows for single-point or scanning measurements, although
the results are limited to surface or near-surface analysis. This method has been successfully used, in combination with NMR, to study sequestering of chromium and molybdenum in nuclear waste glasses.\[25, 26\]

The study of nuclear waste storage materials is not easily solved with any of the above techniques. The presence of a large variety of daughter products in a given waste material requires a bulk sampling technique such as ICP-MS to determine the total sample composition.\[24\] An imaging technique such as SEM can be used to determine bulk structural information, including qualitative measurements of phase separation (either glass-glass or glass-crystalline), crystallite sizes and qualitative chemical analysis. The compositional changes across the surface of the material can be qualitatively characterized by EMPA or a similar technique. These data can be used to indicate domain sizes and compositions within a phase separated sample.

1.3.3 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) has a long history in the study of both amorphous and crystalline materials, as well as success in mixed phase applications. (e.g. references \[18\], \[27\], \[28\]) Solid-state nuclear magnetic resonance is able to probe crystalline and amorphous environments for a single isotope simultaneously. The theory of NMR is discussed in detail in chapter \[2\]
In recent years NMR has made many meaningful contributions to the study of nuclear waste systems. Key crystalline precipitates common to a variety of model nuclear waste systems were identified through a combination of $^{133}$Cs and $^{23}$Na magic-angle spinning (MAS) NMR.\cite{6, 7} Substitution of chromium for molybdenum in the observed crystalline inclusions was successfully measured using $^{133}$Cs MAS NMR.\cite{25, 26} The decomposition of crystalline waste forms after exposure to decay effects has been successfully measured and estimated by $^{29}$Si NMR.\cite{9} $^{95}$Mo MAS NMR has been successfully applied to several structural studies of model nuclear waste glasses.\cite{29, 31}

1.3.4 High-temperature nuclear magnetic resonance

Considering the temperatures used in both the production of nuclear waste storage materials and the elevated temperatures due to the radiation, ambient temperature studies are of limited applicability. Although NMR is the ideal tool for the study of these materials, the application of NMR at high temperatures (>100°C) requires specialized equipment. As will be discussed in future sections, (chapters 2 and 3), NMR at high temperatures results in decreased signal and increased thermal noise.\cite{32} Much of the early research in high-temperature NMR (HT NMR) focused on the design and implementation of HT NMR probes, especially those with the capacity for magic-angle spinning.\cite{33}
1.3.5 Development of the HT NMR Methods

Some of the earliest HT NMR results were obtained in 1958 with the observation of the $^{205}$Tl resonance in various molten salts at temperatures upwards of 500°C.\cite{34}

These experiments used a variable field magnet built around a ceramic furnace with the sample encased in an evacuated ampule wrapped in a radio-frequency coil for continuous wave observation. With the introduction of Fourier-transform NMR, superconducting magnets replaced the previous electromagnets. The implementation of high-temperature experiments in these new magnets required careful engineering, both due to the increased field and the possibility of heat damage to the magnet. Stebbins et al. designed a probe in the 1980’s which implemented a shuttle mechanism, transporting the sample via compressed air from a furnace, located external to the magnet, into probe for data collection.\cite{35, 36} Although this design resulted in the collection of data at very high temperatures ($\geq$1,000°C) the spectra were limited to short non-spinning acquisitions and showed a temperature drop of approximately 10°C from the point of ejection from the furnace to the acquisition time.\cite{36} Other non-spinning high-temperature probes have also been presented in the literatures, typically involving an insulated probehead with a non-magnetic heating coil inserted directly in the magnet.\cite{37, 38} These designs were prone to excessive levels of thermal noise, as the coil was heated together with the sample.
1.3.6 Magic-angle spinning HT NMR

Magic-angle spinning (MAS) is employed in solid-state NMR to enhance the spectral resolution by reducing the linewidths through partial (or complete) averaging of the various anisotropic interactions (see chapter 2). MAS probes utilize high-pressure air streams to levitate a sample container (the rotor) and rotate it at a high velocity at a specific angle relative the magnetic field.[32] High temperature MAS NMR was first accomplished by insulating the probe head and driving the rotor with high temperature N₂.[39–41] Unfortunately, this design results in excessive heating of the NMR coil, increasing the thermal noise.

1.3.7 Containerless HT NMR

Massiot et al. developed a new type of HT NMR probe in 1990.[42, 43] This design utilized an externally located 125 W CO₂ laser as a heat source. The beam was guided into the probe within the magnet bore and directly onto the sample, in this case, lithium sodium sulfate.[43] The sample was compressed into a pellet and inserted into a levitation chamber in the probe above an air stream. As the sample is melted with the laser, the air stream causes it to levitate within the chamber which is encompassed in a saddle-coil, allowing for NMR observations at and above the melting point.[43] This design and its successors were successfully applied to several studies of glass melts of various compositions, particularly calcium aluminates.[42, 44, 46] These probes have somewhat limited capacities, as
the samples must be at or above their melting temperatures for them to “float”. Additionally, due to the observation of these spectra above the melting point, vaporization is a concern in some samples.\cite{47}

1.3.8 Future of HT MAS NMR

Studies employing high-temperature NMR continue to expand from their initial focus on instrumental design, to answering specific questions about structure and chemistry at elevated temperatures. The prevalence of HT NMR as a technique has been greatly aided by the commercialization of several high-temperature probes from companies such as Bruker and Doty Scientific. As entire high-temperature systems are now available for purchase, the pressure on researchers to develop their own systems is relieved, allowing them to focus on the applications.

A recent publication utilizing HT MAS NMR studied the structure of borate melts at elevated temperatures ($\leq 700^\circ$C).\cite{48} Non-spinning HT NMR continues to find its niche, with a recent example of $^{139}$La NMR being used to explore phase transitions in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$.\cite{49} The latest use of high-temperature melt-phase NMR via a levitation probe was applied to the dynamics in lithium borate melts, exploring changes in activation energy with composition.\cite{50}

Although it would be difficult to claim that high-temperature NMR is a common technique, it is definitely one that provides unique data unavailable via other means. The value in HT NMR and its popularity will continue to grow as the
availability of instrumentation improves and the body of literature evolves. Due to the novelty of HT MAS NMR, the available examples have typically focused on pure and homogeneous materials. This work studies both homogeneous and heterogeneous materials at high temperatures.

1.4 Purpose

This study was designed to study the common crystalline devitrification phases found in model nuclear waste storage materials, at both room and elevated temperatures. This work seeks to develop insights into the mechanisms responsible for the devitrification of HLW glasses, particularly by probing the phase distribution of these materials at high temperatures. Information on these phase distributions may potentially provide indications of the sequence of events that lead to the devitrification of these materials.

Chapter 4 initiates this study with an analysis of the $^{133}$Cs, $^{23}$Na and $^{95}$Mo NMR parameters for a range of crystalline molybdate phases. From these data correlations between the structure parameters, from the literature, and our experimental NMR parameters were investigated. Chapter 5 uses high-temperature MAS NMR to study select crystalline phases from chapter 4 by a combination of $^{133}$Cs, $^{23}$Na and $^{95}$Mo MAS NMR up to temperatures of 730°C. A variety of different phase transitions were observed, including a chemical decomposition of one of the crystalline phases, (CsNaMoO$_4$(l)). By establishing the temperature dependence of
these crystalline phases individually, we were then able to study the behaviour of the phases within a glass matrix (Chapter 6). Chapter 6 describes a series of model nuclear waste glasses with different concentrations of molybdenum using both ambient and high temperature $^{133}\text{Cs}$ and $^{23}\text{Na}$ MAS NMR. The phase separation of these materials is shown to be related to a single high-temperature liquid phase, which forms as inclusions in the bulk glass network. The conclusions of chapter 6 have some important implications with respect to the formation of these HLW storage materials, these aspects are discussed in chapter 7.
Chapter 2

Theory

Nuclear magnetic resonance (NMR) is a powerful spectroscopic technique with the ability to probe short-range structure in both ordered and disordered systems. NMR exploits the interaction of the quantum mechanical property spin of a nucleus with an external magnetic field. NMR is sensitive to the small differences in the magnetic field at the nucleus, which can be related to the chemical structure, geometry and dynamics.\[32 \, 51\]

2.1 Spin

Nuclei have a spin quantum number, \( I \), which has a value of \( I = \frac{n}{2} \) where \( n \) is some integer (including 0 and multiples of 2). The spin angular momentum is quantized into \( 2I + 1 \) spin states, labelled by the magnetic quantum number \( m \) which can
take any value in the set \{-I, -(I - 1), ..., I - 1, I\}. Nuclei with even numbers of protons and neutrons have a spin \( I = 0 \); these nuclei can not be observed by NMR, as they have only one spin state. The \( z \)-component of the angular momentum vector is described by a magnetic moment \( \mu_z \), and is a function of the magnetic quantum number and the gyromagnetic ratio \( \gamma \), an intrinsic property of the nucleus.\[32\]

\[
\mu_z = \gamma \hbar m 
\] (2.1)

2.1.1 Zeeman Interaction

The spin states for a given nucleus with \( I > 0 \) are energetically degenerate except in the presence of an external magnetic field \( \vec{B}_0 \). Under \( \vec{B}_0 \) the Zeeman Hamiltonian, \( \hat{H}_z \), describes the energy dependence of the spin states on the magnitude of the magnetic field.

\[
\hat{H}_z |I, m\rangle = E_m |I, m\rangle = -m\hbar\gamma \vec{B}_0 |I, m\rangle 
\] (2.2)

The single-quantum energy difference, \( \Delta E \), for two spin states under the Zeeman interaction is quantified by the angular resonance frequency, \( \omega_0 \).

\[
\Delta E = |\omega_0| = \gamma B_0 
\] (2.3)
The angular resonance frequency is equivalent to the commonly used direct or Larmor frequency, \( \nu_0 = \frac{\omega_0}{2\pi} \). The Larmor frequency is often visualized as the precession of the magnetic moment \( \vec{\mu}_z \) at some angle \( \theta \) around \( \vec{B}_0 \) (Figure 2.1). Typically \( \gamma \) values for most isotopes are sufficiently varied that the Larmor frequencies for any two nuclei are separated by many MHz, figure 2.2. The large energy difference between different isotopes allows for selective excitation through irradiation of the sample at the resonance frequency of the desired nuclide.\cite{32, 51, 52}
Figure 2.1: A vector representation of the magnetization in the two spin states $\alpha$ and $\beta$ for an $I = 1/2$ system
Figure 2.2: The Zeeman splitting is dependent not only on the applied magnetic field, but also the gyromagnetic ratio $\gamma$. Here, three example nuclei: $^1$H (blue), $^{31}$P (green) and $^{89}$Y (orange) show this relationship, as well as the relationship between the Boltzmann distribution and magnetic field (the populations have been exaggerated for emphasis).

2.1.2 Spin $\frac{1}{2}$

A spin $\frac{1}{2}$ nucleus has two Zeeman eigenstates under the influence of $\vec{B}_0$, $|\alpha\rangle = |\frac{1}{2}, \frac{1}{2}\rangle$ and $|\beta\rangle = |\frac{1}{2}, -\frac{1}{2}\rangle$. Classically these can be described as two spins with
\( \vec{\mu}_z \) directed along or against \( \vec{B}_0 \) (Figure 2.1). The energy difference between spin states is small relative to the energy available at ambient conditions, allowing both states to be occupied at equilibrium. The population of spins, or spin density, \( \rho \), in each state is dependent on the magnitude of the energy difference between them and the temperature \( T \). For a spin \( \frac{1}{2} \) system the distribution of populations between the two spin states can be described by equation 2.4 representing the Boltzmann equation.\[^{32}\]

\[
\frac{\rho_\alpha}{\rho_\beta} = e^{-\frac{\Delta E}{kT}} \tag{2.4}
\]

This distribution depends not only on the Boltzmann constant, \( k \), and temperature, \( T \), but also on \( \Delta E \). As \( \Delta E \) is dependent on both \( \vec{B}_0 \) and \( \gamma \) (equation 2.3) the population difference is directly influenced by the magnitude of the employed magnetic field, illustrated by figure 2.2. Physically, equation 2.4 describes a small population difference between the two spin states with a bias for polarization along the magnetic field, i.e. \( \rho_\alpha > \rho_\beta \). From a classical perspective, the larger population of spins in the \( |\alpha\rangle \) state implies a larger number of magnetic moments precessing along \( \vec{B}_0 \). Since the precession about \( \vec{B}_0 \) is random at equilibrium, a collection of superimposed \( \mu_z \) can be pictured as forming a pair of cones along \( z \), with the \( |\alpha\rangle \) cone being slightly larger than the other (Figure 2.1). The projection and sum of these cones on the \( z \)-axis produces a bulk magnetization vector, \( \vec{M}_z \), which, by the Boltzmann equation, is proportional to the strength of the magnetic field.

The magnitude of \( \vec{M}_z \) determines the available signal of a given experiment weighted
by the number of NMR-active spins. In general terms it can be seen that certain nuclei with a large $\gamma$, “high-$\gamma$” nuclei such as $^1$H or $^{31}$P, will always have a greater sensitivity than “low-$\gamma$” nuclei, e.g., $^{73}$Ge or $^{89}$Y, figure 2.2. High-resolution NMR studies of low-$\gamma$ nuclei have only recently become accessible through the advancements in high-field superconducting magnets, where $B_0$ is sufficiently large to provide the necessary sensitivity.

2.1.3 Spin > $1/2$

In systems with spin $I > 1/2$ the population is divided amongst a larger set of spin states, resulting in an inherent reduction in the polarization of the central transition ($|I, \frac{1}{2}\rangle \rightarrow |I, -\frac{1}{2}\rangle$) and decreased sensitivity. Furthermore, the greater spin number indicates a non-spherical charge distribution about the nucleus, making it quadrupolar. The presence of a nuclear quadrupole moment introduces additional effects unique to these nuclei. Specifically, the coupling between the quadrupole moment of the nucleus and the local electric field generated by its charges produces unique NMR characteristics, as is described in section 2.2.3.
2.2 Internal Interactions

Although the Zeeman Hamiltonian describes the largest component of the NMR signal, it is the smaller deviations from the Larmor frequency that allow structural and chemical insights to be made. The observed NMR signal is perturbed away from the Larmor frequency by the additive effect of many different internal interactions due to the chemistry of the sample. Each NMR interaction can be described by a Hamiltonian; those important to this work are outlined below with an effective total Hamiltonian, \( \hat{H}_{\text{tot}} \), described by equation 2.5:

\[
\hat{H}_{\text{tot}} = \hat{H}_Z + \hat{H}_{\text{CS}} + \hat{H}_D + \hat{H}_Q^{(1)} + \hat{H}_Q^{(2)} ...
\]  

(2.5)

where \( \hat{H}_{\text{CS}} \) is the chemical shielding Hamiltonian which describes the influence of electrons in motion on the resonance frequency. Dipolar coupling (\( \hat{H}_D \)) is the product of two nuclear spins interacting through space. The quadrupolar interaction is described by \( \hat{H}_Q \), which is often expanded into its first- and second-order terms (\( \hat{H}_Q^{(1)} \) and \( \hat{H}_Q^{(2)} \) respectively) although higher order effects have been observed in specific cases.\[53, 54\] \( \hat{H}_Q \) affects only spins > 1/2, i.e. quadrupolar nuclei, and is the product of coupling between the electric quadrupole moment (\( Q_m \)) of the nucleus and its surrounding electric field gradient (EFG).
2.2.1 Chemical Shielding

The electrons which surround the nucleus generate their own magnetic field under the influence of the external field. This nuclear magnetic shielding, $\sigma$, can either be additive with $\vec{B}_0$ or opposed, resulting in typically small changes in the observed resonance frequency of the nucleus (Equation 2.6).\cite{32, 52}

\[
\hat{H}_{CS} = \gamma \hbar I \sigma \vec{B}_0
\]

(2.6)

These changes are dependent on the arrangement of the electrons and therefore directly related to the chemistry and structure at the observed nucleus. This is reflected by the magnitude of the $\sigma$ tensor elements. The chemical shielding Hamiltonian is the product of the spin, magnetic field and $\sigma$. In a polycrystalline solid all orientations of the shielding tensor with respect to $\vec{B}_0$ must be considered to be present in any given sampling. This is accomplished by representing $\sigma$ as a second-rank tensor in the principal axis system (PAS).\cite{32}

\[
\sigma = \begin{pmatrix}
\sigma_{XX} & \sigma_{XY} & \sigma_{XZ} \\
\sigma_{YX} & \sigma_{YY} & \sigma_{YZ} \\
\sigma_{ZX} & \sigma_{ZY} & \sigma_{ZZ}
\end{pmatrix}
\]

(2.7)

Experimentally the chemical shielding typically results in a deviation on the order of $\pm 10^3$ Hz from the resonance frequency, although there is a wide nucleus specific
variation. By convention NMR spectra are typically reported by the observed chemical shift, indicated by $\delta$, which is taken as the chemical shielding with respect to the $\nu_0$ of some reference compound.

$$\delta \text{ (ppm)} = \frac{\sigma \text{ (Hz)}}{\nu_0 \text{ (MHz)}} \tag{2.8}$$

The chemical shift in ppm is defined by the three principal tensor components ($\delta_{11} \leq \delta_{22} \leq \delta_{33}$), where the average is referred to as the isotropic shift, $\delta_{iso}$. In solid-state NMR of a powder, the anisotropy of the chemical shift may be observed. This anisotropy is defined by two parameters: the span $\Omega$,

$$\Omega = \delta_{11} - \delta_{33} \tag{2.9}$$

and skew, $\kappa$.

$$\kappa = \frac{3(\delta_{22} - \delta_{iso})}{\delta_{11} - \delta_{33}} \tag{2.10}$$

This chemical shift anisotropy (CSA) results in broad line shapes with inflections that are directly related to the above parameters (Figure 2.3). Lineshape fitting can be used to extract the CSA parameters and determine important structural details on the geometry at the nucleus. The effect of anisotropy on the NMR lineshape are illustrated in figure 2.3. The chemical shielding interaction (and thereby linewidth) is proportional to magnetic field (equation 2.6) making it beneficial to perform experiments with large CSA interactions at lower magnetic
fields to minimize peak broadening.

Figure 2.3: Calculated powder patterns for $^{31}$P NMR with $\Omega = 200$ ppm at $\nu_0 = 83.0$ MHz.
2.2.2 Dipolar Coupling

The precession of a magnetic moment produces a secondary magnetic field which can influence other nuclei in close proximity. The influence through space of one magnetic moment on the magnetic field felt by another is described as *direct dipolar coupling*. Dipolar coupling can be homogeneous, between two identical spins or heterogeneous, between two unlike spins. The dipolar coupling is different in either case, as illustrated below by the secular approximations of $\hat{H}_D$ for the coupling of like spins, (equation 2.11) and for unlike spins, (equation 2.12).

**Homonuclear dipolar coupling:**

$$\hat{H}^{jk}_D(\theta_{jk}) = -\frac{\mu_0}{4\pi} \frac{\gamma_j \gamma_k \hbar}{r_{jk}^3} \frac{1}{2} \left( 3 \cos^2 \theta_{jk} - 1 \right) \left( 3 \hat{I}_{jz} \hat{I}_{kz} - \hat{I}_j \cdot \hat{I}_k \right) \quad (2.11)$$

**Heteronuclear dipolar coupling:**

$$\hat{H}^{jk}_D(\theta_{jk}) = -\frac{\mu_0}{4\pi} \frac{\gamma_j \gamma_k \hbar}{r_{jk}^3} \frac{1}{2} \left( 3 \cos^2 \theta_{jk} - 1 \right) \left( 2 \hat{I}_{jz} \hat{I}_{kz} \right) \quad (2.12)$$

The above equations describe the coupling between two spins, $j$ and $k$, separated by a distance $r_{jk}$ and at an angle $\theta_{jk}$ with respect to $\vec{B}_0$. $\mu_0$ is the Magnetic Constant ($4\pi^{-7} Hm^{-1}$) and $\gamma$ represents the gyromagenetic ratio for the indicated spin.[52] The spin operators for the two spins are represented by $\hat{I}$ and are described in great detail in many popular texts.[32, 52]
**Table 2.1: Spin operators**

| Operator   | Description                        | Operator $|I, m\rangle$                     |
|------------|------------------------------------|-----------------------------------|
| $\hat{I}$  | Nuclear spin                       | $\sqrt{I(I+1)}\hbar |I, m\rangle$                      |
| $\hat{I}_z$| z-component of nuclear spin         | $m\hbar |I, m\rangle$                      |
| $\hat{I}_+ = \hat{I}_x + i\hat{I}_y$ | Raising operator                  | $\sqrt{I(I+1) - m(m+1)}\hbar |I, m+1\rangle$                   |
| $\hat{I}_- = \hat{I}_x - i\hat{I}_y$ | Lowering operator                 | $\sqrt{I(I+1) - m(m-1)}\hbar |I, m-1\rangle$                   |

The direct dipolar Hamiltonian is directly proportional to the magnitude of $\gamma$ for both nuclei involved and inversely dependent on the cube of their internuclear distance. The dependence on $\gamma$ indicates that dipolar coupling is strongest in systems containing nuclei with high resonance frequencies. Dipolar coupling creates additional spin states from the combination of the coupled spins, splitting the observed NMR signal and broadening the range of resonances observed. Often, when the dipolar coupling is weak, the resulting spectrum is simply broadened on the order of $\hat{H}_D$ (typically Hz-kHz). In cases where high-$\gamma$ spins are both highly abundant, increasing the chance possibility of spins being in close proximity, the broadening can limit resolution of multiple sites. The distance dependence for dipolar coupling has been exploited in many studies to derive the interatomic distances through the quantification of $\hat{H}_D$.\[57–59\]

### 2.2.3 Quadrupolar Coupling

Nuclei with $I \geq \frac{1}{2}$ have a non-spherical electric charge distribution, giving rise to an electric quadrupole moment.\[32, 51, 52\] The electric quadrupole moment is typically given as $eQ_m$, where $e$ is the elementary charge. The quadrupole
moment interacts with the local electric field gradient (EFG) produced by the surrounding electric charges described by the tensor $V$, where $V = e\mathbf{q}$. This traceless tensor can be diagonalized by placing it in the principal axis system (PAS) of the interaction.

$$V = \begin{pmatrix} V_{XX} & V_{XY} & V_{XZ} \\ V_{YX} & V_{YY} & V_{YZ} \\ V_{ZX} & V_{ZY} & V_{ZZ} \end{pmatrix}$$

$$V^{\text{PAS}} = \begin{pmatrix} V_{XX} & 0 & 0 \\ 0 & V_{YY} & 0 \\ 0 & 0 & V_{ZZ} \end{pmatrix} \quad (2.13)$$

Where $V_{ZZ} \geq V_{YY} \geq V_{XX}$, and $\sum_i V_{ii} = 0$, allowing the full EFG to be described by any two values. The Hamiltonian for the quadrupole interaction in the PAS of this interaction can be represented as:

$$\hat{H}_Q = \frac{C_Q h}{4I(2I-1)} \left[ 3\hat{I}_z^2 - \hat{I}^2 + \frac{\eta}{2} (\hat{I}_+ + \hat{I}_-) \right] \quad (2.14)$$

where the spin operators are described in table [2.1] and $C_Q$ is the quadrupole coupling constant.

$$C_Q = \frac{e^2 q_{zz} Q_m}{\hbar} \quad (2.15)$$

where the tensor component of the EFG $e q_{zz} = V_{zz}$ of $V^{\text{PAS}}$. The $C_Q$ ranges from zero, for highly symmetric systems, to many MHz. The $C_Q$ is proportional to the largest tensor component, $V_{zz}$, of the EFG, while the other components
are described by the asymmetry parameter $\eta$.\[32\]

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} \quad (2.16)$$

The $C_Q$ is proportional to the magnitude of the quadrupole interaction for a given system and is useful for comparing the interactions of two nuclei of the same spin number. The quadrupole frequency, $\nu_Q$, is a normalization of the $C_Q$ by the spin number, allowing for direct comparison of the magnitude of $\hat{H}_Q$, regardless of spin number.\[32\]

$$\nu_Q = \frac{3C_Q}{2I(I - 1)} \quad (2.17)$$

The Zeeman splitting for a quadrupole nucleus results in more than two degenerate energy levels. The quadrupole interaction results is a perturbation of the Zeeman states which to first order can be defined as:

$$\nu_{(m-1,m)}^{(1)} = \frac{C_Q h}{8I(2I - 1)} \left[ 3 \cos^2 \theta - 1 + \eta \sin^2 \theta \cos 2\phi \right] \left( 3m^2 - I(I + 1) \right) \quad (2.18)$$

where $\theta$ and $\phi$ are the polar coordinates of the PAS with respect to $\vec{B}_0$. The fact that the tensor $V$ is traceless means that under isotropic tumbling, such as in a solution, the interaction will be averaged to zero. In case of a polycrystalline powder the tensors of the spins are statistically distributed relative to $\vec{B}_0$, such that all values of $\theta$ and $\phi$ are present. The resulting NMR resonances of quadrupolar nuclei in a powder are generally a broad signal with a width proportional to the
magnitude of $C_Q$ (Figure 2.4). The total breadth ($\Delta \nu$) of the satellite-transition manifold for a powder pattern broadened by $H_Q^{(1)}$ can be calculated as a simple function of the spin number, $I$ and the quadrupole frequency, $\nu_Q$.

$$\Delta \nu = |1 - 2I| \nu_Q$$  \hspace{1cm} (2.19)

Under the first-order quadrupole interaction spin-states of $|I, \pm m\rangle$ are equally perturbed, therefore transitions are unchanged from their pure Zeeman value. The second-order quadrupole coupling interaction is smaller, proportional to $C_Q^2/\nu_0$, but affects states of $|I, \pm m\rangle$ oppositely and thereby perturbs all the possible single-quantum transitions. (Figure 2.5)

$$\nu_{(m-1,m)}^{(2)} = \frac{C_Q^2}{\nu_0} \frac{1}{32} \left[ (a_1 \cos^4 \theta + b_1 \cos^2 \theta + c_1) (8m(m - 1) - 2) + (a_2 \cos^4 \theta + b_2 \cos^2 \theta + c_2) (4m(m - 1) - 3) \right]$$  \hspace{1cm} (2.20)

where:

$$a_1 = -\frac{n^2}{3} \cos^2 2\phi + 2\eta \cos 2\phi - 3 \hspace{1cm} a_2 = -\frac{n^2}{24} \cos^2 2\phi + \frac{\eta}{4} \cos 2\phi - \frac{3}{8}$$

$$b_1 = \frac{2n^2}{3} \cos^2 2\phi - 2\eta \cos 2\phi - \frac{n^2}{3} + 3 \hspace{1cm} b_2 = \frac{n^2}{12} \cos^2 2\phi - \frac{n^2}{6} + \frac{3}{4}$$

$$c_1 = \frac{n^2}{3} (1 - \cos^2 \phi) \hspace{1cm} c_2 = \frac{n^2}{24} \cos^2 2\phi - \frac{n}{4} \cos 2\phi - \frac{3}{8}$$  \hspace{1cm} (2.21)
Figure 2.4: Calculated powder patterns for $^{23}$Na NMR with a 2 MHz $C_Q$. The broad satellite transitions, ST, show the influence of $H_Q^{(1)}$ while the insets of the central transition, CT, are broadened by the smaller $H_Q^{(2)}$. 

\[
\eta = 1.00, 0.75, 0.50, 0.25, 0.00
\]
Figure 2.5: Diagram of the effect of $\hat{H}_Q$ on the Zeeman energy levels. The effect of $\hat{H}_Q^{(2)}$ on the central transition ($|I, \frac{1}{2}\rangle \rightarrow |I, \frac{1}{2}\rangle$), has been exaggerated for effect.
2.3 NMR spectroscopy

Modern NMR spectroscopy uses superconducting magnets for the $\vec{B}_0$ field, with commercial magnets ranging in strength from 4 to 23 T, producing $^1$H resonance frequencies from 200 to 1000 MHz. Since its discovery in 1938, NMR spectroscopy has been reaching progressively higher magnetic fields, with the earliest examples collected well below 1 T. A typical experimental setup involves a vertical bore magnet with a probe inserted from the bottom which will hold the sample, either loaded from the top of the magnet or preloaded into the probe before its insertion (Figure 2.6). Within the probe, the sample sits within a radio-frequency coil, typically using either a solenoid or saddle design, oriented to deliver pulses perpendicular to $\vec{B}_0$. The probe electronics allow for the resistance and capacitance of the probe circuit to be tuned to the Larmor frequency required for a given experiment. The NMR pulse is synthesized by the externally located spectrometer, a system of amplifiers and synthesizers controlled by a software-driven computer console. The most basic NMR experiment utilizes a pulse synthesized at or very near the resonance frequency of the nucleus of interest, calculated from the Zeeman interaction. The NMR pulse produces a temporary magnetic field, $\vec{B}_1$, perpendicular to $\vec{B}_0$. 
2.3.1 Effect of $\vec{B}_1$

The introduction of a second magnetic field perpendicular to $\vec{B}_0$ causes a time-dependent perturbation of the spin density, changing the distribution between the spin states. From a classical perspective using a two spin-state system, (e.g., $I = \frac{1}{2}$), under the influence of $\vec{B}_1$ there is a continuous change in the number of spins in the $|\alpha\rangle$ and $|\beta\rangle$ states, i.e. with and against $\vec{B}_0$.[52] During the change in spin states the bulk magnetization along $\vec{B}_0$, $\vec{M}_z$ will oscillate between the initial magnitude, $M_0$ and a full inversion of the populations $-M_0$ (Figure 2.7).
Figure 2.7: Representation of the effect of $\vec{B}_1$ on a spin $1/2$ system. The diagram on the left indicates the system at $t = 0$, i.e. before the application of $\vec{B}_1$, while the right indicates the system after a $\pi/2$ pulse. Note that before the application of a $\pi/2$ pulse the spins are in equilibrium, forming a pair of cones. The spin density of each state produces a magnetization vector along $z$, $\vec{M}_\alpha$ and $\vec{M}_\beta$, the sum of which gives the bulk magnetization along $z$, $\vec{M}_z$. After the pulse the spins rotate in synch, producing magnetization in the $x-y$ plane, $\vec{M}_{xy}$.

In addition to changing the populations between the spin states, the $\vec{B}_1$ field also causes the affected spins to precess synchronously. With the spins in synch, the projection of their magnetic moment on the $xy$ plane becomes additive, producing a bulk transverse (with respect to $\vec{B}_0$) magnetization vector, $\vec{M}_{xy}$. At the point where both populations are equal, $\vec{M}_{xy}$ will have a maximum value, while at any point where either population, $\rho_\alpha$ or $\rho_\beta$, is at its maximum value $\vec{M}_{xy}$ will be zero. The sum of the two perpendicular bulk magnetization vectors produces a vector that can take any angle, $\theta$, to $\vec{B}_0$. The degree that the magnetization is tipped
away from \( z \), the "tip angle”, \( \theta \), is dependent on the gyromagnetic ratio of the nucleus, the strength of the \( \vec{B}_1 \) field and the time it was applied, \( \tau_p \).

\[
\theta = -\gamma B_1 \tau_p \tag{2.22}
\]

After the removal of \( \vec{B}_1 \) the spins become free to resume their precession about \( \vec{B}_0 \). Provided \( \vec{M}_{xy} \) is of sufficient magnitude, its precession can induce an observable current in the same NMR coil used to deliver the pulse. The NMR signal is typically collected for some finite time period with the experiment repeated multiple times and the transients from each collection co-added to enhance the signal and average the noise. The observed time-dependent superposition of the precessing spins affected by the \( \vec{B}_1 \) pulse can be Fourier-transformed (FT) from the time domain into the frequency domain, separating distinct signals.\[51\]

The rate at which \( \vec{B}_1 \) rotates the bulk magnetization is termed the \textit{nutation frequency}, \( \nu_{rf} \). We typically quantify \( \nu_{rf} \) for a given \( \vec{B}_1 \) field by determining the pulse length for a \( 2\pi \) tip angle, \( \tau_{2\pi} \) (equation 2.23).

\[
\nu_{rf} = \tau_{2\pi}^{-1} \tag{2.23}
\]

The \( \nu_{rf} \) for the central transition of quadrupolar nuclei in the solid state is affected by the magnitude of \( \nu_Q \).\[32\] In the case where \( \nu_Q >> \nu_{rf} \) the NMR pulse affects only the central transition; while in the case of \( \nu_Q << \nu_{rf} \) all transitions are
effected equally. This effect is dependent on the \( C_Q \) and spin number of the nuclei being studied, of which there may be different types in a single sample. In the case of \( \nu_Q \gg \nu_{rf} \) there is also a decrease in the central transition intensity as more spins populate the satellite transitions. These two effects are demonstrated in figure 2.8. From this figure it can be seen that the maximum for the central transition of a quadrupolar spin can be significantly different than the solution maximum, \( \pi/2_{soln} \). In practice, the nutation frequency for a quadrupolar nucleus is often measured from a reference solution, giving a pulse length maximum, \( \tau_{\pi/2_{soln}} \), for a spin under the \( \nu_Q << \nu_{rf} \) condition. This value can be used to determine an approximate pulse length for the maximum excitation of the central transition, \( \tau_{\pi/2_{CT}} \), of a spin under the \( \nu_Q >> \nu_{rf} \) condition using equation 2.24.

\[
\tau_{\pi/2_{CT}} = \frac{\tau_{\pi/2_{soln}}}{(I + \frac{1}{2})}
\]  

(2.24)
2.3.2 Free-induction decay

At equilibrium, a collection of spins displays a random precession about $\vec{B}_0$, while after $\vec{B}_1$ they will precess with some degree of synchronization. After the removal of $\vec{B}_1$ the small variations in the magnetic field felt by different spins across the sample, either from external or internal sources, cause the spins to lose coherence.
over time. As the precession of the spins becomes asynchronous, the bulk transverse magnetization is lost. This loss in transverse magnetization will be directly proportional to the amplitude of the observable signal. The NMR signal is therefore observed as an oscillating signal with a time-dependent decay, termed the free-induction decay, FID.\textsuperscript{52}

\subsection*{2.3.3 Spin-spin relaxation time, $T_2$}

After the application of $\vec{B}_1$ the spins precess together, but small deviations in the applied magnetic field across the sample cause a continuous loss in coherence. As the precession of the spins becomes asynchronous the bulk transverse magnetization shrinks. The process by which this exponential decay of the bulk transverse magnetization occurs is called \textit{spin-spin} or \textit{transverse relaxation}, quantified by the constant $T_2$ and modelled by the equation \textsuperscript{2.25}

$$M_{xy}(t) = M_0 e^{-t/T_2} \quad (2.25)$$

From equation \textsuperscript{2.25} it can be seen that the amplitude of the magnetization in the $x - y$ plane, $M_{xy}$, at a given time $t$ will decay from the initial magnitude $M_0$ as a function of time, $t$ and $T_2$.\textsuperscript{52} Spin-spin relaxation is influenced both by external effects, such as inhomogeneity in $\vec{B}_0$ and intrinsic effects, such as atomic motion. As the FT of the FID is from the time domain to the frequency domain, systems
with a short $T_2$ time will result in wide spectral signals, and vice versa. After $T_2$ there is no significant bulk magnetization in the transverse plane, but this does not necessarily indicate a return to equilibrium as the build-up of magnetization along $z$ has a separate relaxation mechanism and time constant, $T_1$.

![Figure 2.9: Schematic representation of the loss of magnetization in the $xy$ plane from the effect of spin-spin relaxation.](image)

### 2.3.4 Spin-lattice relaxation time, $T_1$

After the perturbation of the spin system by $\vec{B}_1$ the return to equilibrium and maximum $\vec{M}_z$ occurs exponentially via the process known as the spin-lattice or longitudinal relaxation. The spin-lattice relaxation is quantified by the time constant $T_1$.\cite{32, 51}

$$\frac{M_z(t)}{M_0} = 1 - e^{-t/T_1}$$

(2.26)
The return of the spin system to equilibrium after a pulse follows equation (2.26), where $M_z(t)$ is the magnitude of $\vec{M}_z$ at a given time, $t$, after the pulse and $M_0$ is the maximum magnetization. The spin-lattice relaxation time constant $T_1$ is a useful value for assessing the time required between successive experiments, since after a period of $5 \times T_1 \geq 99\%$ of the bulk magnetization has returned to equilibrium. (Figure 2.10) The build-up of magnetization along the $z$ axis cannot occur without the loss of coherence in the $xy$ plane, therefore $T_1$ must be $\geq T_2$. Spin-lattice relaxation involves the exchange of energy from the polarized spins to its molecular surroundings, typically through conversion into some other form of excited state, e.g. rotation, or vibration.
Figure 2.10: Example of magnetization buildup in a saturation-relaxation experiment following equation 2.26 using a $T_1$ of 100 s. Note that at $5* T_1$ greater than 99% of the magnetization has been recovered.

2.4 NMR of Solids

The anisotropic parts of the various interactions can be used to derive valuable structural information, but they also result in increased lineshape complexity and breadths.[32, 56] In solution and in the gas phase, atoms undergo constant tumbling and translational motion, reducing the interactions to their isotropic values. Solid state NMR can be collected with the sample as a single crystal or as a powder. The study of single crystals uses a goniometer probe head that allows the
crystal to be rotated to any given orientation relative to the magnetic field. Each orientation of the single crystal produces a spectrum of narrow resonances, allowing the anisotropy to be measured over several successive experiments at various orientations. Production of single crystals is often not possible for the majority of solids, especially in sizes sufficient for NMR (at least several milligrams in mass depending on sensitivity). Solids are more commonly examined as a fine powder, which increases the amount of sample that can be packed within the NMR radio-frequency coil and makes the sample preparation simpler. A powder positioned within $\vec{B}_0$ provides a population of statistically orientated nuclei and will produce a predictable pattern for a given set of tensor elements which can be calculated from the Hamiltonians above (see Figures 2.3 and 2.4). These so called “powder patterns” have breadths on the order of the interactions which produce them.[32]

2.4.1 Magic Angle Spinning NMR

The most common method to improve resolution and sensitivity in NMR of solids is “magic” angle spinning (MAS). Typically, MAS is performed on a powder sample loaded into a cylindrical sample holder. Air is pumped through a stator, causing the sample to rotate rapidly at a particular angle to $\vec{B}_0$. (Figure 2.6) The rotation of the sample at an angle of 54.74° results in the averaging of anisotropic interactions possessing a $(3 \cos^2 \beta - 1)$ term; this includes $H_{CS}$, $H_D$, $H_Q^{(1)}$ and partial averaging of $H_Q^{(2)}$. Current commercial probe designs allow for MAS speeds $\leq 70$
kHz, however, reaching these speeds requires very small diameter rotors, i.e. $\leq 1.3$ mm. Current rotor materials and machining technology makes speeds $> 70$ kHz very difficult to reach as these rates approach the sound barrier, placing the rotor under immense force.\textsuperscript{[61]}

### 2.4.2 Spinning Sidebands

The desire for faster spinning speeds is driven by the limitation of MAS to fully average interactions which are greater than the rate of rotation of the sample. In the majority of MAS experiments the spinning frequency, $\nu_r$, is less than the width of the powder pattern and therefore less then the magnitude of the interaction. In solids, large anisotropic interactions, such as $\hat{H}_{CS}$ or $\hat{H}_Q$, cause the spins to resonant over a large range of frequencies. These effects produce broad powder patterns and effectively shorten the time the spins remain in coherence, although, the individual spins retain some transverse magnetization. Under the effect of MAS, coherence is reintroduced at the end of each rotor period, resulting in a train of “spin-echoes”. This extends the duration of the signal in the FID and narrows the observed resonance. Due to the oscillatory behaviour of the FID under MAS, the signal of the broad powder pattern is broken up into repeating spinning sidebands (ssbs) with intensities that approximate the shape of the initial non-spinning pattern. The MAS spectrum has an inherent signal gain over a non-spinning spectrum as it splits the same total signal up among its narrow centerband
and associated ssbs (Figure 2.11).

**Figure 2.11:** Left: Calculated MAS NMR for $^{23}$Na at 10 kHz $\nu_r$ with a $C_Q$ of 500 kHz. Right: CT for $^{23}$Na at 30 kHz $\nu_r$ with a $C_Q$ of 2 MHz.

### 2.4.3 MAS of Quadrupolar Nuclei

Under MAS the second-order quadrupole coupling interaction, $\hat{H}_Q^{(2)}$, depends on two terms $P_2$ and $P_4$, of which only the former is fully averaged under rotation at
the “magic” angle.

\[ P_2(\cos \theta) = \frac{3 \cos^2 \theta - 1}{2} \quad (2.27) \]

\[ P_4(\cos \theta) = \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) \quad (2.28) \]

Rotation at 30.6 or 70.1° will average the \( P_4 \) term but then the first-order interactions will only be partially averaged; therefore it is standard to simply remain at 54.74° and interpret the partially averaged pattern (Figure 2.12).32

![Figure 2.12: Angle dependence of the two terms in \( \hat{H}^{(2)}_Q \).](image)

The effect of \( \hat{H}^{(2)}_Q \) is most prominent for the central transition (CT), \( |\frac{1}{2}\rangle \rightarrow |\frac{-1}{2}\rangle \),
producing distinct centerband patterns under MAS which can be related to the anisotropy at the nucleus. The residual linewidth, $\Delta\nu_{Q}^{(2)}$, of the CT centerband produced by second-order quadrupolar coupling under MAS is dependent on both $C_Q$ and the $\nu_0$ and can be determined by the equation below.\[32\]

$$
\Delta\nu_{Q}^{(2)} = f(I) \frac{C_Q^2 (6 + \eta)^2}{224\nu_0} \tag{2.29}
$$

Where $f(I)$ is a constant dependent on the spin number of the observed nucleus (Table 2.2, Figure 2.11).

The applied MAS rate for a given experiment should ideally be greater than $\Delta\nu_{Q}^{(2)}$ to ensure full separation of the centerband from the sidebands. Fitting the MAS CT centerband provides an accurate method for extracting the quadrupolar parameters. It is generally superior to fitting the non-spinning pattern since the sensitivity is greater under MAS and additional broadening effects from dipolar coupling and CSA can be removed.
2.4.4 Temperature Effects in NMR

Typical solid-state NMR spectrometers and probes are equipped with the capacity for performing experiments between -70 and +150°C. This temperature range is sufficient for many types of studies, but there is interest in studies in both regions above and below these temperatures. NMR at high temperatures is challenging due to the temperature dependence of not only the Boltzmann distribution but also the presence of thermal noise and the increased probability of nuclear motion. There have been significant developments in the field of high-temperature NMR, both in instrumentation and scientific discoveries (see chapter 1).

Low-temperature NMR is also an active area of research, benefiting from enhanced sensitivity. Cryogenic MAS NMR probes have been shown to have several unique applications, with examples of data collection at near liquid helium temperatures (>4K).

The HT NMR of solids can be used to probe phase transitions, either solid-solid or solid-liquid transitions. Solid-solid phase transitions often fall into one of two distinct categories, displacive and order-disorder transitions. Displacive phase-transitions involve a first-order discontinuity in the structural parameters, resulting in a high-temperature phase with structural parameters that can be unrelated to the low-temperature phase. By HT NMR a displacive transition is typically made evident by a change in resonance position, where the position of the high-temperature resonance is unrelated to the low-temperature phase.
In contrast, materials which undergo order-disorder transitions are characterized by a second-order temperature dependence of the cell parameters and atom positions; i.e. the modification of these parameters over the phase transition temperature is continuous to a first-order approximation. In an order-disorder transition the position of the ions in the high-temperature phase must be at positions of related or higher symmetry to those found for the low-temperature phase. The strong symmetry relationship between the site positions in the two phases typically produce NMR spectra with resonances at related positions, e.g. the high-temperature resonance may be at the average position of the low-temperature resonances.[63]

2.4.5 Signal Dependence on Temperature

From equation 2.30 it can be seen that the NMR signal, $S$, is proportional to the product of the number of spins ($n$), volume of the sample ($V_c$), field and $I$ divided by the temperature ($T$) and the Boltzmann constant ($k$).

$$S = \frac{nV_c\gamma^3B_0^2h^2I(I+1)}{3kT}$$

(2.30)

Noise (N) from the probe’s coil can become an issue due to its direct dependence on temperature. The noise from the coil also depends on its resistance ($R_E$) and the
filter bandwidth ($\Delta \omega$), but these are somewhat independent of temperature.\footnote{32}

$$N = (4R_E kT \Delta \omega)^{\frac{1}{2}}$$ \hspace{1cm} (2.31)

From these equations it can be estimated that the NMR sensitivity is proportional to $T^{-3/2}$. Therefore doubling the temperature of an experiment can produce as much as a 65% decrease in signal-to-noise. The MAS NMR probe used in these studies uses direct laser heating of the sample, minimizing the thermal noise in the coil. This design can increase the sensitivity to a maximum of $S/N \propto T^{-1}$.

### 2.4.6 Temperature Effects on Relaxation

Although the above equations suggest that raising the temperature should result in decreased NMR sensitivity, there are several benefits to high-temperature NMR. As temperature increases, the chance for atoms to become mobile increases, resulting in vibrational and even translational motion. Mobility results in the averaging of the orientation-dependent interactions, increasing $T_2$ and narrowing the NMR signal (Figure 2.13). With averaging of the anisotropic interactions, the broad contributions to the NMR spectrum are lost, condensing the signal intensity into the narrowed resonance, improving sensitivity with temperature.

In solids, the increase in temperature also results in a decrease in the spin-lattice
relaxation time, up to the melting point, at which the nuclides undergo full translational motion. Past the melting point $T_1$ begins to increase. The decrease in $T_1$ up to the melting point allows for shorter repetition delays at higher temperatures, making it possible to collect more transients in a given experimental time. The decreased linewidths and experimental delays provide a measure of compensation for the intrinsic decrease in signal at high-temperatures.\[32\]

**Figure 2.13:** Approximation of the temperature effects on relaxation. An approximate location of the melting point ($T_m$) is noted by the red line.
Chapter 3

Experimental Materials and Methods

3.1 Synthesis

All materials were synthesized by either high-temperature solid-state synthesis or crystallization from aqueous solution, except for the commercial sodium molybdate sample (Table 3.1).

3.1.1 \( \text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O} \)

Sodium molybdate dihydrate was crystallized by evaporation of a saturated solution of sodium molybdate. The purity and identity of the crystalline phase were
Table 3.1: List of Materials and Sources

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Synthesized compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cesium Molybdate</td>
<td>Cs$_2$MoO$_4$</td>
<td>High Temperature Synthesis</td>
</tr>
<tr>
<td>Tricesium Sodium Dimolybdate</td>
<td>Cs$_3$Na(MoO$_4$)$_2$</td>
<td>High Temperature Synthesis</td>
</tr>
<tr>
<td>Sodium Molybdate Dihydrate</td>
<td>Na$_2$MoO$_4$·2H$_2$O</td>
<td>Evaporative Crystallization</td>
</tr>
<tr>
<td>Cesium Sodium Molybdate Dihydrate</td>
<td>CsNaMo$_4$·2H$_2$O</td>
<td>Evaporative Crystallization</td>
</tr>
<tr>
<td><strong>Commercial Materials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sodium Molybdate</td>
<td>Na$_2$MoO$_4$</td>
<td>JT Baker, 99.5%</td>
</tr>
<tr>
<td>Molybdenum Trioxide</td>
<td>MoO$_3$</td>
<td>Merck ≥85%</td>
</tr>
<tr>
<td>Sodium Carbonate</td>
<td>Na$_2$CO$_3$</td>
<td>Shawihigwa, 98%</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>B(OH)$_3$</td>
<td>Analar, 99.5%</td>
</tr>
<tr>
<td>Cesium Carbonate</td>
<td>Cs$_2$CO$_3$</td>
<td>Kawecki Berylco Industries Inc, 99.5%</td>
</tr>
<tr>
<td>Silicon dioxide</td>
<td>SiO$_2$</td>
<td></td>
</tr>
</tbody>
</table>

confirmed by comparison of the $^{23}$Na MAS NMR spectrum at 14.1 T with the known NMR parameters from the literature.\footnote{32}

### 3.1.2 Cs$_2$MoO$_4$

Cesium molybdate synthesis was prepared with molybdenum trioxide and cesium carbonate. Reagents were intimately mixed in a 1:1 molar ratio using a mortar and pestle, then heated in a box furnace in an alumina crucible. Decarbonation was achieved by heating at 420°C for 12 hrs. The reaction mixture was heated to 725°C for 4 hours and then slowly cooled to 375°C for 12 hours. Crystalline
purities of \( \geq 98\% \) were determined by powder X-ray diffraction (XRD) and \(^{133}\text{Cs}\) MAS NMR.

### 3.1.3 CsNaMoO\(_4\)·2H\(_2\)O

Cesium sodium molybdate dihydrate was prepared by saturation and evaporation of a 1:1 (molar) aqueous solution of sodium molybdate and cesium molybdate. Samples were found to be \( \geq 98\% \) pure by XRD and \(^{133}\text{Cs}\) MAS NMR.

### 3.1.4 Cs\(_3\)Na(MoO\(_4\))\(_2\)

Tricesium sodium dimolybdate is a novel compound synthesized by the high temperature reaction of cesium carbonate, molybdenum trioxide and sodium molybdate. The materials for Cs\(_3\)Na(MoO\(_4\))\(_2\) were first decarbonated at 420°C for 12 hrs. Samples were then heated to 725°C for 4 hrs, cooled to 550°C for 1 hr, then 375°C for 12 hrs and finally 200°C for 1 hr. This process was repeated multiple times (2–4) for each sample to increase the purity above 95%. The analyzed samples were determined to be \( \geq 98\% \) by integration of the \(^{133}\text{Cs}\) MAS NMR spectra.
3.1.5 \( \text{Na}_2\text{Mo}_2\text{O}_7 \)

Sodium dimolybdate was synthesized from a mixture of sodium carbonate and molybdenum trioxide. The mixture was decarbonated at 550°C for 12 hrs. The sample was then heated for 24 hrs at 600°C. Sample purity was confirmed using \(^{23}\text{Na}\) MAS NMR and XRD.

3.1.6 Model Nuclear Waste Glasses

The well-studied French nuclear waste glass “SON68” was used as the basis for the synthesis of these model glasses (Table 3.2). The main focus of this work is the behaviour of crystalline molybdates in these glass systems, therefore SON68 was simplified from a >28-oxide glass to a five-oxide glass. Glasses CM3, CM5 and CM10 were designed to have 3, 5 and 10 mole % \( \text{Cs}_2\text{O} \) and 2.5, 5 and 10 mole % \( \text{MoO}_3 \), respectively, before normalization. The ratio of \( \text{B}_2\text{O}_3 : \text{SiO}_2 \) was held constant for CM5 and CM10 glasses, while the CM3 glass used a different ratio.

Mixtures of the required carbonates and oxides were decarbonated at 550°C for 12 hrs. The cesium carbonate content in the batch mixture was increased by 150% from the target concentration. This is a procedure that was developed in our lab to compensate for the well documented volatility of cesium at temperatures above 1100°C.\(^{[4][66]}\) Samples were heated at 1300°C for one hour in platinum crucibles. CM5 and CM10 glasses were cooled at a rate of 60°C/hr, similar to the expected
cooling rate in industrial applications. CM3 was quenched from 1300°C to room temperature in ice water, in order to minimize the crystallinity in the sample.

Table 3.2: Glass compositions

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SON68</th>
<th>CM3</th>
<th>CM5</th>
<th>CM10</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52.27</td>
<td>62.0</td>
<td>64.6</td>
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<tr>
<td>B₂O₃</td>
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<td>16.5</td>
<td>17.2</td>
<td>15.8</td>
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<tr>
<td>Na₂O</td>
<td>11.05</td>
<td>16.0</td>
<td>9.4</td>
<td>4.0</td>
</tr>
<tr>
<td>Cs₂O</td>
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<td>3.0</td>
<td>5.2</td>
<td>10.4</td>
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<tr>
<td>MoO₃</td>
<td>0.82</td>
<td>2.5</td>
<td>5.2</td>
<td>10.4</td>
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<tr>
<td>CaO</td>
<td>5.00</td>
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<td>-</td>
</tr>
<tr>
<td>Li₂O</td>
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</tr>
<tr>
<td>Al₂O₃</td>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZnO</td>
<td>2.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>1.49</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
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<td>NiO</td>
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<td>BaO</td>
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<td>Cr₂O₃</td>
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<td>-</td>
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<tr>
<td>Pr₂O₃</td>
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<tr>
<td>SrO</td>
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<td>-</td>
<td>-</td>
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</tr>
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</tr>
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<td>CoO</td>
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</tr>
<tr>
<td>TeO₂</td>
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</tr>
<tr>
<td>Y₂O₃</td>
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<td>-</td>
</tr>
<tr>
<td>SnO₂</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>&lt; 0.01</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
3.2 X-ray Diffraction

Sample purity was confirmed by X-ray diffraction courtesy of the Bieringer research group (University of Manitoba). A Bragg-Brentano powder X-ray diffractometer (PANalytical X’Pert Pro, diffractometer radius = 240 mm) was used, employing Cu K$_{\alpha 1,2}$ radiation ($\lambda = 1.54098$ Å, 1.544426 Å) equipped with a diffracted beam Ni-filter and an X’Celerator detector. Data sets were collected in the 2$\theta$ range 10$^\circ$ to 90$^\circ$ in 0.0083$^\circ$ steps using a zero-background quartz sample holder.

3.3 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Simultaneous TGA/DTA experiments were conducted using a LINSEIS L81 Thermogravimetric analyzer in vertical measurement arrangement, courtesy of the Bieringer research group. Samples with masses of 47-49 mg were placed in alumina crucibles and heated at a rate of 10$^\circ$C per minute. Measurements for Cs$_3$Na(MoO$_4$)$_2$ were collected from 25$^\circ$C to 1200$^\circ$C, while CsNaMoO$_4$·2H$_2$O was collected up to 400$^\circ$C. All experiments were performed in flowing oxygen (6 L/min). Buoyancy corrections were applied to all samples.
3.4 NMR Methodology

NMR experiments were performed on either a Varian UNITYINOVA 600 spectrometer with an Oxford 14.1 T magnet or on a Bruker Avance III 400 spectrometer with a 9.4 T wide-bore magnet. At 14.1 T, the NMR probes used to collect the spectra were a 5 mm double-resonance probe and 1.6 mm triple-resonance probe, capable of $\nu_r \leq 12$ and 38 kHz, respectively. The 9.4 T spectrometer is equipped with a 7 mm high-temperature MAS wide-bore probe capable of $\nu_r \leq 3.5$ kHz. Additionally, an adapter was built so that a 4 mm single-channel low-gamma MAS probe from a narrow-bore 11.7 T spectrometer ($\nu_r \leq 15$ kHz) could be used.

3.4.1 Single Pulse Experiments

The majority of the experiments performed were single-pulse (a.k.a. Bloch decay) experiments (figure 3.1). This sequence uses a single radio-frequency pulse with a given amplitude to produce a transverse magnetic field, $B_1$. The duration of this pulse can be calibrated to give a desired tip angle to the bulk magnetization. A short delay follows the pulse to allow the spectrometer to switch from transmitting to receiving mode. This delay must often be increased to some time greater than the acoustic ringing of the radio-frequency coil; for low-gamma nuclei this dead time can be $> 50\mu$s. After each application of the pulse sequence a relaxation delay is inserted to allow the spin system to return to equilibrium. (see section 2.3.4)
Using short tip angle pulses with the Bloch sequence, as opposed to $\pi/2$, has the advantage of providing wider excitation bandwidth, due to the short pulse duration; while also requiring shorter recycle delays, since the magnetization is less perturbed. The dependence of recycle delays on pulse angle was shown by Ernst’s equation for optimum tip-angle (Equation 3.1), where the pulse angle $\theta$ is shown to have an exponential relationship to the minimum necessary recycle delay, $T_{RD}$ and the $T_1$.

\[
\cos \theta = e^{-\frac{T_{RD}}{T_1}}
\]  

(3.1)

This can be further illustrated by the figure 3.2 where the recycle delay increases exponentially as the tip angle approaches 90°, but is relatively linear at smaller angles. For experiments with long $T_1$s, utilizing a small tip angle ($\leq 30^\circ$) can allow for the collection of a much greater number of transients relative to a $\pi/2$
Figure 3.2: Dependence of net magnetization (Red) and minimum relaxation delay (Blue) on the pulse tip angle. These curves were calculated from Ernst’s equation 3.1 for a system with a $T_1 = 100s$. The curve for magnetization can be taken as proportional to the available signal in a single experiment at the selected tip angle.

experiment, in the same time period. By applying pulses with tip angles between 30 and 60° as much as 50% of the maximum signal is achieved, but requires $\leq \frac{1}{5}$th the recycle delay. This is optimal for experiments with low sensitivity and long $T_1$’s, (e.g., $^{95}$Mo).
3.4.2 Saturation Recovery Experiments

The measurement of $T_1$ at different temperatures can provide insight into the dynamics of nuclei. $T_1$ is measured by using either an inversion-recovery or saturation-recovery experiment, with the former having a greater dynamic range but being significantly slower to collect than the latter. The saturation-recovery experiment, (Figure 3.3), was chosen for its speed and the fact that the $T_1$s for $^{133}$Cs are typically long therefore do not require the precision of the inversion-recovery experiment. In this pulse sequence, a series of $\pi/2$ pulses is rapidly applied to ensure all the magnetization is “saturated” into the $x−y$ plane. After the magnetization is sufficiently saturated, the system is left to relax for some time, $\tau$. Relaxation mechanisms cause magnetization to grow along $z$. By applying another $\pi/2$ pulse after $\tau$, the magnetization that has relaxed is rotated into the observable $x−y$ plane, while any remaining magnetization in the $x−y$ plane is rotated along $z$. The observed signal represents the spins in the sample that were relaxed during $\tau$, and is a direct measurement of $\vec{M}_z$ at this point in the relaxation.
profile (see figure 2.10 and section 2.3.4). By plotting the intensity of the signal as a function of $\tau$, $T_1$ may be determined from equation 2.26.

3.4.3 Experimentation at 14.1 T

All MAS NMR experiments at 14.1 T were Bloch-decay experiments used for characterizing the quadrupolar powder patterns and isotropic shifts for the various materials. The tip angles used for the experiments were kept in the quantitative region, between 10 and 15°. $^{23}$Na and $^{133}$Cs MAS NMR experiments utilized the 1.6 mm TR MAS probe, rotating small powdered samples (10 to 30 mg) at a rate of 30.000 ± 0.002 kHz, to ensure maximum separation between the centerbands and their sidebands. $^{95}$Mo MAS NMR was typically performed with the 5 mm DR MAS probe to obtain the maximum sample mass ($\leq$ 150 mg), using $\nu_r$ of 8.000 ± 0.005 kHz. Recycle delays ranged from 1 to 5 seconds for $^{23}$Na and $^{95}$Mo experiments (under short tip angle acquisitions), while $^{133}$Cs NMR required delays between 20 and 130 s. The $B_1$ fields for the various experiments varied from a $\nu_{rf}$ of 19 kHz for $^{95}$Mo, and 71 kHz $^{133}$Cs up to 111 kHz for $^{23}$Na. NMR spectra were collected relative to 1.0 M NaCl(aq) for $^{23}$Na, 2.0 M Na$_2$MoO$_4$(aq) for $^{95}$Mo, and 0.1 M CsCl(aq) for $^{133}$Cs.
3.4.4 Ambient temperature experimentation at 9.4 T

The majority of the NMR experiments at 9.4 T were performed at high temperature and are described below (Section 3.5). Additional $^{95}$Mo MAS NMR experiments were collected on a narrow-bore single-channel low-gamma 4 mm MAS probe using $\leq 100$ mg of sample. Spectra were collected with $\pi/2_{\text{solid}}$ pulses, using $\nu_r$ of 10 kHz and $\nu_{rf}$ of 26 kHz. The larger tip angle used in these 9.4 T experiments provided a necessary increase in sensitivity relative to the 14.1 T data, but also required longer recycle delays of up to 30 seconds, (see figure 3.2). $^{95}$Mo spectra were collected with 1,024 to 5,120 co-added transients.

3.4.5 Fitting NMR spectra

NMR parameters were determined by fitting the spectra using simulation software. Both the Wsolids and Dmfit simulation packages were employed.67 68 Fitting of the slow spinning $^{23}$Na MAS NMR data was accomplished using the QUASAR solid-state simulation package implemented within DMfit 2011.69 $^{133}$Cs MAS NMR was fit with a series of hybridized Gaussian/Lorentzian lineshapes to produce simulations of best fit using DMfit.
3.5  High-temperature experimentation at 9.4 T

Nuclear magnetic resonance experiments were collected at temperatures ranging from 21°C to 730°C using a high-temperature 7 mm MAS NMR double-resonance (H/F-X) probe (details below). The specialized probe design allows for a decrease in the expected thermal noise at high temperatures. Calibration procedures were developed to ensure a temperature accuracy within the probe of ±20-50°C (section 3.5.2).

High temperature rotors were loaded with 20-40 mg of sample in an AlN insert, which was spun at $\nu_r$ between 2.5 and 3.5 kHz. The 50 W CO$_2$ laser wattage was calibrated to the internal temperature of the rotor by observation of $^{79}\text{Br}$ MAS NMR of KBr, with a reproducibility of ± 20°C. Spectra were collected at temperature intervals of either 50 or 100°C, with a 6 to 8 minute equilibrium time allowed before each new temperature collection. The tuning range of the 7 mm HT MAS probe was lowered with a 360 db shunt to reach the range of $\nu_0$ for $^{95}\text{Mo}$ (26.06 MHz). Both Bloch and saturation-recovery experiments were performed, applying $\nu_{rf}$ between 30 ($^{95}\text{Mo}$) and 90 ($^{23}\text{Na}$) kHz.

3.5.1  7 mm HT MAS NMR probe

Many different high-temperature probe designs have been shown in the literature, employing a variety of heat sources (see chapter 1). The 7 mm HT MAS
probe developed by Bruker uses an aluminum nitride or boron nitride insert held within a modified zirconia rotor by a pair of Macor rings (Figure 3.4). The outer rotor has a hole in the base through which a laser is directed at the insert, and the ceramic distributes the heat evenly throughout the sample. A specially designed stator holds the rotor at the magic angle and contains the solenoid radio-frequency coil. The stator coil and probe are cooled by the bearing and drive nitrogen gas used to rotate the sample. The probe is held within a 9.4 T wide-bore magnet with a 50 W laser positioned below the magnet on an optical rail, allowing careful manipulation of the laser’s position relative the magnet. There is a mirror at the end of the laser guide which directs the beam into the probe, where a second mirror directs the beam to approximately the magic angle and incident on the rotor assembly. A titanium thermocouple is attached to the mirror to monitor the ambient temperature in the probe and to ensure no stray laser power is being scattered. The 7 mm HT MAS NMR probe is rated for approximately 700-800°C, although achieving these temperatures depends on the stability of the sample under MAS.

The high-temperature experiments performed with this probe must be monitored continuously for both safety and experimental reasons. Additionally, prolonged operation of the system at high-temperatures increases the risk of MAS instability and failure of the probe. For these reasons our experiments were typically limited to a total time at high-temperatures (>200°C) of ≤8 hours per day.
3.5.2 Temperature Calibration of HT-MAS NMR

The temperature at the rotating sample is isolated from the rest of the probe by the cooling action of the bearing air, making it impossible to have an electronic temperature probe in the rotor. Therefore the temperature must be determined by NMR using an external standard. These are compounds which have known and predictable spectral changes that occur with temperature. The most common NMR temperature probe is $\delta_{iso}^{(207)\text{Pb}}$ in lead nitrate (Pb(NO$_3$)$_2$), which shows a linear relationship of $0.775 \pm 0.007$ ppm / °C for temperatures up to 300°C.\cite{70}

This relationship was shown to be second order when extended up to 400°C with...
a relationship of $T = -5.2 \times 10^{-4} \delta^2 + 1.3 \delta + 30.1$, although the former linear relationship is still more commonly used.\cite{71, 72} Unfortunately lead nitrate has a melting point of 470°C, making it only effective as a probe for approximately half the temperature range of the 7 mm HT MAS probe.\cite{73}

The second most common temperature probe is the $^{79}$Br NMR signal of potassium bromide (KBr), where $\delta_{iso}$ changes linearly at a rate of $-0.0249 \pm 0.0015$ ppm / °C.\cite{72} The temperature trend for KBr is an order of magnitude less sensitive than Pb(NO$_3$)$_2$, but has the benefit of providing linear behaviour up to its melting point at 734°C. This allows for calibration of the full temperature range of the 7 mm MAS probe.\cite{73} Calibrations were done for both Pb(NO$_3$)$_2$ and KBr with increasing laser power to within 50°C of their respective melting points. The linear relationship between the temperature calculated from the observed chemical shifts and the laser power was used as a calibration. It was found through multiple trials with KBr, which has a relatively narrow resonance even at high temperature, that the temperature for a given laser setting is accurate to within ±20°C (Figure 3.5). Although this accounts for the error in the external system, the temperature within the rotor is also sensitive to sample size, density and thermal properties.

From the observation of the phase transitions in Na$_2$MoO$_4$ by $^{23}$Na NMR and the $^{207}$Pb NMR signal of Pb(NO$_3$)$_2$ above 300°C it appears that the samples can have temperature gradients approaching 50°C across the sample volume. This gradient is typically smaller than the measurement error in small sample sizes, but has led to some variance between experimental trials.
Figure 3.5: Example calibration curve using both KBr and (Pb(NO$_3$)$_2$). Temperature is calculated from the position of the $\delta_{iso}$ observed using either the relationship of 0.775 ppm $/ ^\circ$C ($^{207}$Pb) or -0.0249 ppm $/ ^\circ$C ($^{79}$Br).
Chapter 4

Characterization of Crystalline Molybdates

The complexity of the mixed-phase precipitates in vitreous high-level liquid waste storage materials makes them difficult to analyze by bulk techniques such as XRD. NMR has the advantage of looking at each nucleus in the system individually, simplifying the number of phases observed in a single analysis.[65] The NMR parameters for a nucleus in a crystalline compound are typically sufficiently unique that the phases can be directly identified from their lineshapes. By parameterizing the NMR characteristics of pure alkali molybdates, their presence in complex multiphase materials, such as HLW storage materials, can be readily identified and quantified from the “fingerprint” of their characteristic lineshapes. Furthermore, from studying trends in the NMR parameters of molybdates, it may be possible to
derive insight into the identity and structure of uncharacterized phases that may be encountered spectroscopically.

The most common molybdate precipitates in model vitreous HLW materials are Na$_{2}$MoO$_{4}$, Na$_{2}$MoO$_{4}$$\cdot$2H$_{2}$O, Cs$_{3}$Na(MoO$_{4}$)$_{2}$ and CsNaMoO$_{4}$$\cdot$2H$_{2}$O. The presence of cesium sodium molybdate dihydrate and sodium dihydrate indicate that water can penetrate these materials. Cs$_{3}$Na(MoO$_{4}$)$_{2}$ was previously characterized in the literature by MAS NMR, although little is known about its crystal structure. In certain model waste glass compositions both Na$_{2}$Mo$_{2}$O$_{7}$ and Cs$_{2}$MoO$_{4}$ have been observed; the crystal structures of both these phases are well characterized in the literature. Na$_{2}$Mo$_{2}$O$_{7}$ was previously characterized by $^{23}$Na MAS NMR, but its $^{95}$Mo NMR characteristics are unknown.

### 4.1 Results

Seven crystalline molybdate materials were synthesized (with the exception of commercial Na$_{2}$MoO$_{4}$) and characterized by the combination of $^{23}$Na and $^{133}$Cs MAS NMR at 14.1 T, and $^{95}$Mo MAS NMR at both 9.4 and 14.1 T. Sample purity and identity were confirmed by powder XRD, except for Cs$_{3}$Na(MoO$_{4}$)$_{2}$ which was confirmed by $^{133}$Cs MAS NMR.

The structural parameters of each cation in these materials, (Cs, Na, Mo), were collated from the crystallographic data available in the literature. M–O bond
lengths for the three cations was collected and analyzed for all the studied materials. The bond angles for Mo and Na were also assembled. The Cs–O polyhedra are large and distorted, therefore, the bond angles were not determined.

NMR parameters for each crystalline material were determined by simulating the spectra and determining the parameters of best fit (see section 3.4.5). Our results were found to be within error of previously reported results (Table 4.1).
### Table 4.1: NMR Parameters in Crystalline Alkali Molybdates

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{23}$Na MAS NMR</th>
<th>$^{133}$Cs MAS NMR</th>
<th>$^{95}$Mo MAS NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta_{iso}$ (ppm)</td>
<td>$C_Q$ (MHz)</td>
<td>$\eta$</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$</td>
<td>3.2 ± 0.1</td>
<td>2.59 ± 0.01</td>
<td>0.0</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$·2H$_2$O</td>
<td>-1.4 ± 0.05</td>
<td>0.88 ± 0.1</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td>Cs$_2$MoO$_4$</td>
<td>4.1 ± 0.2</td>
<td>2.68 ± 0.03</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>Cs$_3$Na(MoO$_4$)$_2$</td>
<td>-11.8 ± 0.1</td>
<td>0.73 ± 0.02</td>
<td>0 ± 0.1</td>
</tr>
<tr>
<td>CsNaMoO$_4$·2H$_2$O</td>
<td>-0.4 ± 0.3</td>
<td>1.33 ± 0.02</td>
<td>1</td>
</tr>
<tr>
<td>Na$_2$Mo$_2$O$_7$</td>
<td>-5.9 ± 0.02</td>
<td>1.44 ± 0.01</td>
<td>0.53 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>-9.9 ± 0.01</td>
<td>2.57 ± 0.02</td>
<td>0.16 ± 0.02</td>
</tr>
</tbody>
</table>
4.1.1 $^{23}$Na MAS NMR

$^{23}$Na NMR is a common technique for the study of chemical structure largely because of its favourable spectroscopic characteristics. $^{23}$Na ($I = \frac{3}{2}$) is the single naturally occurring isotope of sodium and features a relatively high $\gamma$, yielding a resonance frequency of 158.8 MHz at 14.1 T. The chemical shift range of $^{23}$Na is relatively narrow while the quadrupole moment is moderate (104 mb), often resulting in broad and overlapped lineshapes and making resolution of multiple sites challenging, (Figure 4.1). The $^{23}$Na $\delta_{iso}$ for this series of molybdates ranged between 4.1 to -11.8 ppm. $C_Q$’s varied between 730 kHz to 2.68 MHz, with asymmetry parameters, $\eta$, from 0 to 1.
Figure 4.1: $^{23}$Na MAS NMR at 14.1 T of a. Na$_2$MoO$_4$, b. Na$_2$MoO$_4$$\cdot$2H$_2$O, c. Cs$_2$MoO$_4$, d. Cs$_3$Na(MoO$_4$)$_2$, and e. Na$_2$Mo$_2$O$_7$. Experimental spectra are in black, simulated fits are in red.
4.1.2 $^{133}$Cs MAS NMR

$^{133}$Cs ($I = \frac{7}{2}$) has a moderate $\gamma$ (78.69 MHz at 14.1 T) and is the only naturally occurring isotope of cesium. The quadrupole moment of $^{133}$Cs is very small (-3.4 mb) while the chemical shift range is large, often producing narrow, well-separated centerbands in MAS NMR spectra. Due to the high polarizability of cesium electron density, $^{133}$Cs NMR powder patterns are often broadened by a significant CSA. Typically, a lack of second-order quadrupole broadening of the $^{133}$Cs centerband under MAS requires that the quadrupole coupling constant be determined by the breadth of the spinning sideband manifold using equation (2.19).

$^{133}$Cs $\delta_{iso}$ were found to range from -144 to 161 ppm, with $C_Q$’s of 160 to 370 kHz (Figure 4.2).
Figure 4.2: $^{133}\text{Cs}$ MAS NMR of a. $\text{Cs}_2\text{MoO}_4$, b. $\text{CsNaMoO}_4\cdot2\text{H}_2\text{O}$, and c. $\text{Cs}_3\text{Na} (\text{MoO}_4)_2$. Spectra i were collected at 3 kHz (a and c) and 10 kHz (b) MAS at 9.4 T for sideband analysis. Spectra ii are focused on the $^{133}\text{Cs}$ centerbands (indicated with *) collected using 30 (a and c) and 20 (b) kHz MAS at 14.1 T. (Note the unmarked ssb in bii.)
4.1.3 $^{95}$Mo MAS NMR

$^{95}$Mo ($I = \frac{5}{2}$) is one of two NMR-active isotopes of molybdenum with a natural abundance of 15.92%. $^{95}$Mo NMR is typically chosen over $^{97}$Mo NMR due to the smaller quadrupole moment (-22 mb and 255 mb, respectively) and higher abundance (15.72 vs. 9.46%). Due to the moderately low $\gamma$ of both isotopes (39.3 MHz and 40.14 MHz, respectively) sensitivity can be an issue. $^{95}$Mo $\delta_{iso}$ for the studied materials were determined to range between -32.5 and 8 ppm. $C_Q$’s were determined to lie between 0 and 1.26 MHz, with $\eta$ of 0.13 to 1 (Figure 4.3).
Figure 4.3: $^{95}$Mo MAS NMR of a. Na$_2$MoO$_4$, b. Na$_2$MoO$_4$·2H$_2$O, c. Cs$_2$MoO$_4$, d Cs$_2$MoO$_4$, e. Cs$_3$Na(MoO$_4$)$_2$ and f. Na$_2$Mo$_2$O$_7$ at 14.1 T. Experimental spectra are in black, simulated fits are in red.
4.2 Discussion of Individual Crystalline Phases

4.2.1 Na$_2$MoO$_4$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure_image}
\caption{Structure of Na$_2$MoO$_4$. The positions of molybdenum ions are indicated in purple, sodium in yellow and oxygen in red.}
\end{figure}

Na$_2$MoO$_4$ forms in a well studied cubic unit cell (Figure 4.4).[74] The sodium ions occupy a single site located at a special position with axial symmetry. The observed $^{23}$Na MAS NMR lineshape has $\eta = 0$, consistent with the observed structure (Table 4.1, Figure 4.1). The single molybdenum site in the structure is at a position of perfect $T_d$ symmetry with the surrounding oxygens. The $^{95}$Mo MAS NMR of Na$_2$MoO$_4$ is notable for having a single site with a $C_Q$ of 0.
4.3), this was confirmed by $^{97}$Mo MAS NMR at 9.4 T where the couplings would be an order of magnitude larger (not shown).

4.2.2 $\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O}$

Sodium molybdate dihydrate has an orthorhombic unit cell, with two sodium and one molybdenum site (Figure 4.5). One of the sodium cations coordinates to two water molecules and three molybdate ($\text{MoO}_4^{2-}$) units in a trigonal bipyramidal
arrangement. The other sodium coordinates to four molybdates and two water molecules in an octahedral geometry. It was found in the literature that the octahedral site produces a $^{23}\text{Na}$ lineshape with a $C_Q$ of 0.88 MHz, while the five-coordinate site results in a $C_Q$ of 2.68 MHz (Figure 4.1).\cite{76}

The $^{95}\text{Mo}$ MAS NMR of Na$_2$MoO$_4$·2H$_2$O produces a single resonance with a moderate $C_Q$ of 1.15 MHz. The $^{95}\text{Mo}$ cations are coordinated to four oxygens at bond lengths varying between 1.75 to 1.78 Å. The asymmetry between the Mo-O bonds is consistent with the observed $^{95}\text{Mo}$ $\eta$ of 0.82 and $C_Q \neq 0$.\cite{76}
4.2.3 $\text{Na}_2\text{Mo}_2\text{O}_7$

Sodium dimolybdate has two crystallographically distinct sodium sites, one with near-octahedral coordination and the other coordinated to eight oxygens (Figure 4.6).\cite{77} The eight-coordinate site has Na-O bonds ranging from 1.86 to 2.79 Å, while the octahedral site has a smaller bond length range of 1.92 to 2.45 Å. The $^{23}\text{Na}$ MAS NMR spectrum shows two distinct lineshapes, with 1:1 intensity, consistent with the crystal structure (Figure 4.1).
There are two molybdenum sites in the Na$_2$Mo$_2$O$_7$ crystal structure with equal occupancy (Figure 4.7). One of the sites is four coordinate with Mo-O bond lengths between 1.71 and 1.784 Å. The O-Mo-O angle for this site varies from 106 to 111°, resulting in low $C_5$ site symmetry. The other site is six-coordinate, with four short Mo-O bonds of either 1.68 or 1.90 Å in length, and two longer bonds of 2.27 Å. The resulting O-Mo-O bond angles range between 78.5 and 104.2°, producing local $C_2$ point-group symmetry.

The $^{95}$Mo MAS NMR spectra of the two molybdenum sites are completely overlapped, (Figure 4.3 and 4.8). Using the combination of $^{95}$Mo MAS NMR data at 14.1 T and 9.4 T a plausible fit was produced. The fit was restricted to two sites in a 1:1 integrated ratio, with each site having distinctly different $\eta$. The simulations in figure 4.8 appear to satisfy the above restrictions and provide a satisfactory fit.
Figure 4.8: $^{95}$Mo MAS NMR of Na$_2$Mo$_2$O$_7$ at two different fields. Site 1 was simulated with $\delta_{iso} = -25.2$ ppm, $\eta = 0.13$ and $C_Q = 1.2$ MHz. Site 2 was simulated with $\delta_{iso} = -22.9$, $\eta = 0.95$, and $C_Q = 1.26$ MHz (Table 4.1).

to the experimental data at both fields using identical NMR parameters ($\delta_{iso}$, $C_Q$ and $\eta$). The 9.4 T data have some discrepancy between the experiment and fit, which can be corrected by reducing the high-$\eta$ site by 20% in intensity. This correction is likely required due to the difference in nutation frequencies between the two sites, due to their different $C_Q$’s and the difference in pulse tip angle between the experiments, (15° at 14.1 T and 90° at 9.4 T). The high-$\eta$ site is tentatively assigned to the four-coordinate site, due to its lower symmetry, while the higher symmetry site was assigned to the six-coordinate site.
4.2.4 \( \text{Cs}_2\text{MoO}_4 \)

\textbf{Figure 4.9:} Structure of \( \text{Cs}_2\text{MoO}_4 \). The positions of molybdenum ions are indicated in purple, cesium in green and oxygen in red. The two cesium sites have been labelled as Cs(1) and Cs(2).

\( \text{Cs}_2\text{MoO}_4 \) forms an orthorhombic unit cell with cesium ions in a 1:1 ratio (Figure 4.10)\(^{[78, 79]} \) One cesium cation is asymmetrically coordinated to 10 oxygens at Cs-O bond distances between 2.95 and 3.65 Å. The second site has a more ordered local geometry and coordinates 9 oxygens with Cs-O bond lengths of 3.05 to 3.60 Å. \(^{133}\text{Cs} \) MAS NMR of \( \text{Cs}_2\text{MoO}_4 \) has two distinct sites at 51 and -15 ppm (Figure 4.2). The integrated intensities of the two central transition centerbands at 30 kHz MAS and 14.1 T gives a ratio of 3:2. The difference between the crystallographic
data and the NMR data is attributed to the loss of intensity for the low frequency site to its ssb manifold. The $C_Q$ was estimated for each site from the breadth of the spinning sideband manifold. The sidebands for the higher frequency site (51 ppm) covered a range of 81 kHz, indicating a $C_Q$ of approximately 190 kHz. The second site (-15 ppm) had sidebands which covered a range of 96 kHz, indicating a $C_Q$ of 220 kHz. The higher intensity site at higher frequency is consistent with the crystal structure as typically higher coordination spheres result in increased NMR chemical shifts.[80]

The molybdenum NMR shows a single resonance, consistent with the structure, which has a single MoO$_4^{2-}$ site with near-tetrahedral symmetry. The Mo-O bond lengths varied between 1.77 and 1.78 Å. The bond angles also have a fairly small range, from 108.5 to 110.1°. The small variance in structural parameters is consistent with the relatively small $C_Q$ (480 kHz), although the lack of point-group symmetry is reflected in the high $\eta$ of 1.
4.2.5 CsNaMoO$_4$·2H$_2$O

CsNaMoO$_4$·2H$_2$O has an orthorhombic unit cell with Na$^+$ ions in octahedral symmetry (Figure 4.10). The sodium ions are coordinated to two MoO$_4^{2-}$ units at axial positions, with four water molecules coordinated equatorially. The weakly octahedral symmetry is consistent with the moderate $C_Q$ (1.33 MHz) observed in the $^{23}$Na MAS NMR (Figure 4.1, Table 4.1). The low point-group symmetry for the sodium ions is consistent with the strong asymmetry in the NMR, as observed by the $\eta = 1$ lineshape.
The cesium ions are located in large cavities in the structure, coordinating a total of eleven oxygens either in molybdate units or water. The Cs–O bond distances range between 3.13 and 3.80 Å, although an additional six oxygen atoms are within the same cavity in the structure, at interatomic Cs–O distances between 4.06 and 4.86 Å. The single cesium site produces a $^{133}\text{Cs}$ NMR resonance that is only a few ppm broad under MAS. The MAS centerband has no second-order quadrupolar lineshape, therefore, the $C_Q$ was assigned by measuring the breadth of the spinning sideband manifold. Assuming the ssbs are primarily the product of the first-order quadrupolar interaction, the $C_Q$ was measured as 220 kHz, from a ssb manifold breadth of 96 kHz, (Figure 4.2).

The single molybdenum site has near-tetrahedral symmetry, with O-Mo-O bond angles of either 110 or 108°. Three of the Mo-O bond lengths are approximately 1.76 Å, with a fourth longer bond of 1.78 Å. The distorted tetrahedral geometry is consistent with the relatively high asymmetry ($\eta = 0.75$) observed in the $^{95}\text{Mo}$ MAS NMR (Figure 4.3).
4.2.6 Cs$_3$Na(MoO$_4$)$_2$

![Structure of K$_3$Na(MoO$_4$)$_2$](image)

**Figure 4.11**: Structure of K$_3$Na(MoO$_4$)$_2$. This structure was used as a structural basis for the interpretation of the NMR data for Cs$_3$Na(MoO$_4$)$_2$. The positions of molybdenum ions are indicated in purple, potassium in blue, sodium in yellow, and oxygen in red.

The Cs$_3$Na(MoO$_4$)$_2$ crystal structure is unknown, although a possibly analogous dimolybdate, K$_3$Na(MoO$_4$)$_2$, has been studied in the literature (Figure 4.11). From $^{133}$Cs MAS NMR it was determined that there are two sites in the Cs$_3$Na(MoO$_4$)$_2$ structure with an approximately 2:1 ratio. The two sites were found to have significantly different $C_Q$s, with the higher frequency and higher integrated intensity site (161 ppm) having a $C_Q$ of approximately 160 kHz, while the lower frequency
site (-144 ppm) is almost double that at 370 kHz (Table 4.1). This ratio is consistent with the ratio of potassium sites in K$_3$Na(MoO$_4$)$_2$, where one K$^+$ is positioned at the corners of the pseudo-hexagonal unit cell, while two equivalent K$^+$ sites are within the centre of the structure, suggesting the phases may be isostructural.

The $^{23}$Na MAS NMR of Cs$_3$Na(MoO$_4$)$_2$ has a single resonance with a moderate quadrupole coupling of 0.73 kHz and $\eta$ of zero (Figure 4.1, Table 4.1). The $^{23}$Na lineshape is broadened, with poorly resolved inflections when compared to the other molybdates. This appears consistent with the proposed K$_3$Na(MoO$_4$)$_2$ structure, which has a single sodium site with local $D_{3d}$ point group symmetry. Any rotation axis greater than $C_2$ requires that the EFG produce an $\eta$ of zero.[56]

The $^{95}$Mo MAS NMR spectrum of Cs$_3$Na(MoO$_4$)$_2$ has a single resonance which was fit to a moderate $C_Q$ of 650 kHz, with an $\eta$ of 0.0. The single molybdenum site in K$_3$Na(MoO$_4$)$_2$ is four-coordinate, with a point group symmetry of $C_{3v}$. This is consistent with the observed $\eta$ of zero, for the reasons stated above. The $^{23}$Na, $^{133}$Cs and $^{95}$Mo MAS NMR spectra strongly suggests that Cs$_3$Na(MoO$_4$)$_2$ and K$_3$Na(MoO$_4$)$_2$ are isostructural.

4.3 Structural Trends in Molybdates

In the sodium-cesium-molybdate crystalline system, the observed $^{23}$Na, $^{133}$Cs and $^{95}$Mo NMR parameters are primarily influenced by the interaction of these cations
with their adjacent oxygen atoms, producing possible correlations between symmetry and lineshape. Measuring the anisotropic interactions (CSA and quadrupolar interactions) for an NMR site often lends insight into the point-group symmetry for the given ion. Assessing the structural distortions for a given site is somewhat arbitrary, with several different models used in the literature.\cite{55} Correlation of the difference between the maximum and minimum metal–oxygen distance has been shown to provide a fairly robust correlation with NMR parameters in oxide systems.\cite{55} The statistical variance in interatomic distances and bond angles for a given site have also been shown to influence the NMR signal in covalently bonded oxides.\cite{83} The statistical variance for these compounds was calculated from the sum of the square of the difference between each data point, \(x\), and the average, \(\bar{x}\), divided by the population, \(n\), (Equation 4.1).

\[
\text{Variance} = \frac{\sum (x - \bar{x})^2}{n - 1} \tag{4.1}
\]

### 4.3.1 \(^{23}\text{Na}\) NMR of Molybdates

Sodium cations form ionic bonds with oxygen with a range of Na–O bond distances between 1.8 – 2.9 Å. The sodium ions in these compounds coordinate with between 5 and 8 oxygens, with the majority of the crystalline phases having sodium sites with pseudo-octahedral symmetry. Trends between the structural parameters and \(^{23}\text{Na}\) NMR parameters were explored using a variety of structural
Figure 4.12: **Top**: $^{23}$Na $C_Q$ compared to Na–O bond length variance. **Middle**: $\eta$ compared to the difference between maximum and minimum Na–O bond length. **Bottom**: dependence of $\delta_{\text{iso}}$ on average Na–O bond distance. Structural and $^{23}$Na NMR data for the studied molybdates are represented in blue. Additional points include Na$_6$Mo$_{10}$O$_{33}$ (red), Na$_2$WO$_4$ and Na$_2$WO$_4$·2H$_2$O (orange). The linear trend in the bottom plot has an $R^2 = 0.91$. 
parameters; some examples are shown in figure 4.12. The Na–O bond lengths and associated structural parameters were determined from the crystallographic structures reported in the literature.\cite{74, 75, 77} Additionally, the maximum and minimum Na–O bond distances were determined for each sodium site, as well as the difference between them. The sampling of crystalline molybdate phases studied was relatively small, therefore the \( ^{23} \text{Na} \) parameters for \( \text{Na}_6\text{Mo}_{10}\text{O}_{33} \), \( \text{Na}_2\text{WO}_4 \) and \( \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \) from the literature were added to the data set.\cite{25, 76, 84, 85} Sodium tungstates form isostructural and isoelectronic crystalline phases with their molybdate analogues, therefore the structural dependence of the \( ^{23} \text{Na} \) NMR parameters should be similar.\cite{76}

A reasonable correlation (\( R^2 = 0.91 \)) was found between the average Na–O bond distance and \( ^{23} \text{Na} \) isotropic shift, (Figure 4.12). This is consistent with the trends found for several other NMR nuclei, in addition to being a recognized trend in glass.\cite{80, 86, 87} This decrease in \( \delta_{\text{iso}} \) with increasing interatomic distance is attributed to the decreasing influence of the oxygen on the \( ^{23} \text{Na} \) shielding as the distance between them increases, reducing the chemical shift closer to that of the unshielded nucleus.

It was found that the \( ^{23} \text{Na} C_Q \) and \( \eta \) showed weak or no correlations with the Na–O bond length parameters that were tested (Figure 4.12). The lack of correlation amongst these parameters is likely related to their dependence on symmetry, which is poorly measured from the Na–O bond lengths. More appropriately an analysis
of the bond angles between Na–O sites may produce better correlations, but the lack of symmetry in many sites makes assigning bond angles arbitrary.

### 4.3.2 $^{133}$Cs MAS NMR Trends

The structural trends for Cs$^+$ in cesium molybdates were challenging to assign because of the difficulty identifying the cesium coordination number. Some Cs$^+$ sites had possible Cs–O contacts with upwards of 17 oxygens, with bond lengths between 2.95 and 4.86 Å. When assigning trends it was found that limiting the Cs$^+$ coordination sphere to interatomic Cs–O distances of $< 4$ Å provided the most satisfying correlations. Of the three cesium molybdates studied, only two of the crystal structures are known, CsNaMoO$_4$·2H$_2$O and Cs$_2$MoO$_4$, limiting the analyzed data set to three points, (as there are two Cs$^+$ sites in Cs$_2$MoO$_4$). The structure of K$_3$Na(MoO$_4$)$_2$ was used to tentatively extend the data set, by assuming its isostructurality with Cs$_3$Na(MoO$_4$)$_2$. The K–O bond lengths for this structure were converted to Cs–O bond lengths by the ratio of Cs$^+$/K$^+$ radii. Shannon radii were used for each cation under the appropriate coordination numbers, 10 and 12. [88]
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Figure 4.13: Correlations of $^{133}$Cs $\delta_{iso}$ for cesium ions in Cs$_2$MoO$_4$, and CsNaMoO$_4$·2H$_2$O crystalline phases, (blue). Two additional points (green) were added to the data set using the $^{133}$Cs NMR parameters for Cs$_3$Na(MoO$_4$)$_2$ and the modified K$_3$Na(MoO$_4$)$_2$ structure parameters, (see text). Linear trendlines are in green. The correlation of $\delta_{iso}$ with the minimum, maximum and average interatomic distance gives poor correlations, $R^2 = 0.51$, 0.54, and 0.07, respectively. The correlation between the statistical variance of Cs–O interatomic distances and $\delta_{iso}$, is notably strong, $R^2 = 0.94$. Errors are within the squares.

The statistical variance of the interatomic Cs–O distance appears to have a strong correlation, $R^2 = 0.94$, with $\delta_{iso}$ (Figure 4.13). The variance acts as a measure of the asymmetry of the Cs$^+$ cavity, which is expected to have a strong correlation to the asymmetry of the CSA and EFG tensors. From the analysis of the total data set there appears to be weak correlations, $R^2 \approx 0.5$, between $\delta_{iso}$ and the
minimum and maximum Cs–O bond length for a given site, (Figure 4.13). The variance and difference between minimum and maximum Cs–O bond distances were also studied (not shown), but were not as conclusive as the trends in figure 4.13. The average Cs–O distance was found to have no correlation, $R^2 = 0.07$, with $\delta_{iso}$, unlike the trend found with $^{23}$Na NMR above. This is likely a product of the weaker Cs–O interactions, whereas in $^{23}$Na there are fewer coordinating oxygens, producing stronger and more measurable effects of the Na–O distance on $\delta_{iso}$. Due to the longer distance between the Cs$^+$ and oxygen, and the larger coordination numbers, the effect of a single oxygen on the chemical shielding is expected to be reduced. Therefore, the correlations between the measurement of a single Cs–O bond length and the overall change in $\delta_{iso}$ is small, while the variance is a measurement which approximates the total coordination of the Cs$^+$ ion.
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**Figure 4.14:** Correlations of $^{133}\text{Cs } C_Q$ for cesium ions in $\text{Cs}_2\text{MoO}_4$, and $\text{CsNaMoO}_4\cdot2\text{H}_2\text{O}$ crystalline phases (blue). Two additional points (green) were added to the data set using the $^{133}\text{Cs}$ NMR parameters for $\text{Cs}_3\text{Na(MoO}_4)_2$ and the modified $\text{K}_3\text{Na(MoO}_4)_2$ structure parameters (see text). Linear trendlines are in green. The correlation of $C_Q$ with the average interatomic distance gives a weak correlation, $R^2 = 0.45$. The correlation between the $C_Q$ and the maximum, minimum and statistical variance of Cs–O interatomic distances are notably stronger, $R^2 = 0.74, 0.93$ and 0.82, respectively.

The minimum Cs–O distance has a strong positive correlation with the $^{133}\text{Cs } C_Q$, $R^2 = 0.93$ (Figure 4.14). The maximum Cs–O distance also shows a complementary, although weaker, positive correlation, $R^2 = 0.74$. The oxygen atoms are strongly charged anions and will thereby have a large influence on the EFG of the $^{133}\text{Cs}$ nucleus. The closest oxygen is expected to have the strongest effect, as
this interatomic distance is the most direct measure of the minimum interaction between the two ions. The positive correlations of bond distance and $C_Q$ suggests that the magnitude of the interaction between the Cs$^+$ cation and its adjacent oxygen anions is the primary effect dictating the magnitude of the electric field gradient. In addition to the interatomic distances, it is expected that the overall asymmetry of the Cs$^+$ site in the crystalline phase will have some effect on the shape and magnitude of the EFG. This is supported by the presence of a relatively strong correlation between the $^{133}$Cs $C_Q$ and the variance in Cs–O distance, which is effectively a measure of the disorder at the Cs$^+$ site. In addition, the increase in $C_Q$ with Cs–O variance is consistent with the above suggestion that both CSA and the EFG increase across the series. The presence of fairly strong correlations with the inclusion of the Cs$_3$Na(MoO$_4$)$_2$ data act as a further indication that this phase is isostructural with K$_3$Na(MoO$_4$)$_2$.

4.3.3 $^{95}$Mo MAS NMR Trends

Molybdenum(VI) is a high-field strength cation, (see chapter 1), causing the majority of its oxides to be limited to either isolated anionic tetrahedral MoO$_4^{2−}$ units or chained octahedral motifs, with the former being the more common in the phases under investigation. The exception is Na$_2$Mo$_2$O$_7$ which has molybdenum arranged in chains of octahedral and tetrahedral moieties. It was found that the octahedral site of Na$_2$Mo$_2$O$_7$ consistently fell outside any plausible correlations
based on MoO$_4^{2-}$, therefore, it was removed from the data set. Although, the $^{133}$Cs MAS NMR for Cs$_3$Na(MoO$_4$)$_2$ could be predictably added to the series using modified structural parameters for K$_3$Na(MoO$_4$)$_2$ (section 4.3.2) the effect of exchanging Cs$^+$ for K$^+$ on the structure of the MoO$_4^{2-}$ unit cannot be as easily predicted. Therefore, the data set did not incorporate the $^{95}$Mo MAS NMR data from the Cs$_3$Na(MoO$_4$)$_2$ phase, due to the unknown structure.

![Graphs](image.png)

**Figure 4.15:** Correlations between $^{95}$Mo $\delta_{iso}$ and various structural parameters for the tetrahedral molybdenum sites in Na$_2$MoO$_4$, Na$_2$MoO$_4$·2H$_2$O, Na$_2$Mo$_2$O$_7$, Cs$_2$MoO$_4$, and CsNaMoO$_4$·2H$_2$O. $R^2$ values for the applied linear trendlines were determined, (left to right, top to bottom): 0.79, 0.88, 0.96 and 0.95.

The $C_Q$ is the most sensitive $^{95}$Mo NMR parameter with respect to the structural measurements studied, showing the strongest correlations (Figure 4.15). This is
largely the result of the $C_Q$ being dependent on a single tensor element of the EFG, thereby making it a direct measurement of the magnitude of the EFG in one dimension. Perfect tetrahedral geometry has cubic symmetry, therefore a quadrupolar nucleus with this symmetry would have a $C_Q$ of 0, since the electric field gradient is symmetrical in all directions. Therefore, any deviation of a $^{95}$Mo site from pure $T_d$ symmetry results in notable changes in $C_Q$ and $\eta$.

The Mo-O bond distances yield the weakest correlations with $C_Q$, $R^2 = 0.79 - 0.88$, compared to the bond angle measurements, $R^2 = 0.95 - 0.96$. The weakness of the bond length correlations is due to these measurements only being good metrics in the case where the $V_{ZZ}$ tensor component (the EFG tensor component which determines $C_Q$) is coincident with the bond. Notable from these relationships is that as the Mo-O bond length decreases, there is a consistent increase in the $C_Q$.

The change in bond angles provide a superior correlation with $C_Q$ since it is a more direct measurement of the distortion at the molybdenum site. Similar correlations between $C_Q$ and bond angle have been observed in covalent systems.\[89\] [90]
Figure 4.16: Correlations between $^{95}$Mo $\delta_{iso}$ and various structural parameters for the tetrahedral molybdenum sites in Na$_2$MoO$_4$, Na$_2$MoO$_4$·2H$_2$O, Na$_2$Mo$_2$O$_7$, Cs$_2$MoO$_4$, and CsNaMoO$_4$·2H$_2$O. $R^2$ values for the applied linear trendlines are (left to right, top to bottom): 0.09, 0.36, 0.44 and 0.74. Error in $\delta_{iso}$ is within the area of the data points.

The $^{95}$Mo $\delta_{iso}$ appears to be largely insensitive to the Mo–O bond distance, although the dynamic range of bond lengths is much smaller than in the other studied cations, (1.76 to 1.79 Å) (Figure 4.16). There appears to be a very weak correlation between the maximum Mo–O bond distance and the isotropic shift, but the spread is significant. The variance in O-Mo-O bond angle shows a weak correlation with $\delta_{iso}$, indicating a relationship between $\delta_{iso}$ and the deviation from tetrahedral symmetry. The correlation is even stronger, $R^2 = 0.74$, between the
maximum bond angle and $\delta_{iso}$. These correlations with bond angles suggest that the origin of the chemical shift differences amongst the molybdates may be due to changes in the anisotropy of the chemical shielding tensors. Since the changes in Mo–O bond distances between phases are very minimal the total shielding of the nucleus is likely similar. The largest difference between molybdenum sites is the variation in bond angles, which indicates differences in adherence to tetrahedral symmetry, implying changes in the symmetry of the shielding tensors. Conceptually, similar trends between the magnitude of the chemical shift tensors with structural disorder have been observed in many examples in the literature.\cite{26}

To confirm the source of the changes in $\delta_{iso}$, quantum chemical calculations and non-spinning $^{95}$Mo NMR would be required to better characterize the full $^{95}$Mo shielding tensors, both of which are outside the scope of this study.
Characterization of Crystalline Molybdates

Figure 4.17: Correlations between $^{95}\text{Mo }\eta$ and various structural parameters for the tetrahedral molybdenum sites in Na$_2$MoO$_4$·2H$_2$O, Na$_2$Mo$_2$O$_7$, Cs$_2$MoO$_4$, and CsNaMoO$_4$·2H$_2$O. $R^2$ values for the applied linear trendlines are (left to right, top to bottom): 0.001, 0.0003, 0.20 and 0.63.

Poor correlation is observed between the asymmetry parameter, $\eta$, and any of the structural metrics used, (Figure 4.17). For a Mo$^{6+}$ ion in near-tetrahedral geometry, at most, a single tensor element of the EFG may be oriented along a Mo–O bond. This is contrary to other geometries, such as octahedral, where there are perpendicular bonds which may be coincident with the EFG tensor components. Therefore, the structural metrics employed in figure 4.17 are expected to poorly measure $\eta$, as they are effectively indicators of the tetrahedral geometry, which can not be co-linear with the EFG tensor principal components. The weak correlation
between the average O-Mo-O angle and $\eta$ is consistent with this assessment, as this measurement assesses the internuclear space, where at least two of the EFG shielding tensor components are directed.

4.4 Conclusions

Nuclear magnetic resonance spectroscopy is a powerful tool for the characterization of crystalline molybdates. $^{23}$Na MAS NMR is a highly informative technique, but is prone to significant overlap in the case of multiple sites. The large $^{23}$Na quadrupole couplings and small chemical shift range common to molybdates can make them challenging to study. The chemical shift of $^{23}$Na in molybdates shows a notable correlation with the average Na–O interatomic distance, providing a useful indicator for estimating the size of the Na$^+$ site in novel molybdate phases. $^{133}$Cs MAS NMR of these molybdates is notable for its narrow centerbands and wide chemical shift dispersion. It was found that the asymmetry in the Cs$^+$ site results in decreases in chemical shift and increases in the $^{133}$Cs $C_Q$. $^{95}$Mo NMR parameters were shown to have relatively strong correlations to structure in the studied phases. The $C_Q$ of $^{95}$Mo is particularly sensitive to the Mo–O bond lengths and asymmetry at the Mo$_6^+$ site in these molybdates. Furthermore, the structure of the crystallographically uncharacterized phase Cs$_3$Na(MoO$_4$)$_2$ was shown to have NMR parameters consistent with the analogous K$_3$Na(MoO$_4$)$_2$ structure.
Chapter 5

High Temperature MAS NMR of Sodium and Cesium Molybdates

The goal of this work is to develop an understanding of the high temperature behaviour of the crystalline molybdate phases commonly found as precipitates in model high-level waste materials. Two of the phases, Cs$_2$MoO$_4$ and Na$_2$MoO$_4$, have well understood crystal structures that have been characterized at high-temperature by a variety of techniques. The two mixed-alkali molybdate phases, CsNaMoO$_4$·2H$_2$O and Cs$_3$Na(MoO$_4$)$_2$, have not been characterized at non-ambient temperatures.
5.1 Methods

$^{23}\text{Na}$ and $^{133}\text{Cs}$ MAS NMR data were acquired for the four compounds, $\text{Cs}_2\text{MoO}_4$, $\text{Na}_2\text{MoO}_4$, $\text{Cs}_3\text{Na} \,(\text{MoO}_4)_2$ and $\text{CsNaMoO}_4 \cdot 2\text{H}_2\text{O}$ at temperatures ranging from 21 to 730°C. $^{95}\text{Mo}$ MAS NMR was used to explore specific high-temperature phases, however full high-temperature profiles were not characterized due to the inherently low sensitivity of $^{95}\text{Mo}$.

5.2 $\text{Na}_2\text{MoO}_4$

$\text{Na}_2\text{MoO}_4$ has four known phases that occur between room temperature and its melting point at 682°C.[74, 84] These phases have been previously identified using high-temperature XRD in combination with TGA-DTA.[74, 84] In this work we have labelled these phases from the highest-temperature phase to the room-temperature phase as $\alpha$–, $\beta$–, $\gamma$–, $\delta$–$\text{Na}_2\text{MoO}_4$. In the literature the structures of the high-temperature phases $\alpha$– and $\beta$–$\text{Na}_2\text{MoO}_4$ were determined by Rietveld refinement.[84] The diffractogram of $\gamma$–$\text{Na}_2\text{MoO}_4$ was too disordered to be refined, although in a previous study the unit cell was determined.[74]

5.2.1 HT $^{23}\text{Na}$ MAS NMR of $\text{Na}_2\text{MoO}_4$

$^{23}\text{Na}$ MAS NMR spectra of $\text{Na}_2\text{MoO}_4$ were acquired incrementally over a temperature range of 21°C to 730°C. At temperatures around 730°C the presence of liquid
Na$_2$MoO$_4$ was observable in the $^{23}$Na spectrum, limiting MAS NMR spectra to below this temperature (Figure 5.1). Four distinct lineshapes were observed over this temperature range and the parameters from fitting these spectra are collected in table 5.1. The phases observed by NMR correspond to the phase transitions observed in the literature by high-temperature XRD (Figure 5.1).

<table>
<thead>
<tr>
<th>Phase</th>
<th>$T_{XRD}$ (°C)</th>
<th>$T_{NMR}$ (°C)</th>
<th>$C_Q$ MHz</th>
<th>$\eta$</th>
<th>$\delta_{iso}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>22</td>
<td>21</td>
<td>2.6</td>
<td>0</td>
<td>3.2 ± 0.1</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>498</td>
<td>500</td>
<td>1.96</td>
<td>0.9</td>
<td>-10.2 ± 0.4</td>
</tr>
<tr>
<td>$\beta$</td>
<td>598</td>
<td>600</td>
<td>1.82</td>
<td>1</td>
<td>-10.6 ± 0.4</td>
</tr>
<tr>
<td>$\alpha$ (two sites)</td>
<td>654</td>
<td>675</td>
<td>2.1</td>
<td>1</td>
<td>-6.8 ±0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.2</td>
<td>1</td>
<td>-8.7 ±0.2</td>
</tr>
<tr>
<td>Melt</td>
<td>682</td>
<td>700</td>
<td>–</td>
<td>–</td>
<td>-8.3 ± 0.1</td>
</tr>
</tbody>
</table>

Table 5.1: HT $^{23}$Na MAS NMR parameters for Na$_2$MoO$_4$
**Figure 5.1:** $^{23}$Na MAS NMR of $\text{Na}_2\text{MoO}_4$ as a function of temperature. These spectra are representative of the “purest” lineshapes attained for the four HT phases of $\text{Na}_2\text{MoO}_4$, over several trials.
Figure 5.1 shows the $^{23}$Na MAS NMR of Na$_2$MoO$_4$ over the range of temperatures studied. Figure 5.2 shows the progressive transformation between the $\delta$-Na$_2$MoO$_4$ and $\gamma$-Na$_2$MoO$_4$ phases. The spectra were collected in increments of ≤ 50°C from room temperature to 730°C. The spectra in figure 5.1 were selected from this data set to be representative of the lineshapes for the high-temperature phases of Na$_2$MoO$_4$. At temperatures between each spectra in figure 5.1 the lineshapes could be convoluted by the overlap of multiple phases, this is visible in figure 5.2.

Between 21°C and 200°C there is a progressive broadening of the two second-order quadrupole effect (SOQE) inflections in the $^{23}$Na lineshape. Upon further heating up to 480°C the spectrum becomes progressively narrower and gaussian-shaped, suggesting the $^{23}$Na atom is undergoing increased motion, resulting in averaging of the SOQE. At ≈480°C the $\gamma$-Na$_2$MoO$_4$ lineshape becomes visible, overlapping with the lower temperature $\delta$-phase. The decrease in symmetry at the sodium site observed in the HTXRD and evidenced by the increase in $\eta$ in the high-temperature $^{23}$Na MAS NMR, is consistent with a reversible displacive phase transition.\cite{63}

Upon heating to 600°C the $\gamma$-Na$_2$MoO$_4$ phase undergoes a transformation to the $\beta$-Na$_2$MoO$_4$ phase. This change is noted by a small contraction in the lineshape, characterized by a change in $C_Q$ from 1.96 to 1.82 MHz (Figure 5.1 and Table 5.1). Both $\gamma$- and $\beta$-Na$_2$MoO$_4$ had been determined to have orthorhombic unit cells, with the latter structure being solved by Rietveld refinement.\cite{84} Without a solved structure it can only be speculated that based on the NMR results the
change in symmetry at the Na\textsuperscript{+} site must be slight for the asymmetry to remain consistent between the two phases. The small deviation in peak position between the two phases (\(\gamma, \beta\)) may indicate a second displacive phase transition, but the similar symmetry is more consistent with an order-disorder transition.\textsuperscript{[63]}

The \(\alpha\)-Na\textsubscript{2}MoO\textsubscript{4} phase is observable at 675\(^\circ\)C, but is convoluted with the lower
temperature $\beta$-$\text{Na}_2\text{MoO}_4$ (Figure 5.1). Upon reaching 700°C, the $^{23}\text{Na}$ lineshape for $\alpha$-$\text{Na}_2\text{MoO}_4$ is well resolved. The structure of this high-temperature phase was determined from powder XRD, and consists of two partially occupied $\text{Na}^+$ sites either within or on the edges of the hexagonal unit cell (Figure 5.4). Each sodium is in pseudo-octahedral coordination, with relatively long Na–O bonds of 2.72-2.76 Å. The increase in site distortion between the $\beta$- and $\alpha$-phases is consistent with a displacive transition, further evidenced by the change in $\delta_{iso}$.
between the two phases. Due to the presence of two known sites from the XRD data, the $^{23}\text{Na}$ MAS NMR spectrum of $\alpha$-Na$_2$MoO$_4$ was fit to two sites of equal intensity, each with an $\eta$ of 1 (Figure 5.4). The melt has a chemical shift at -8.3 ppm, situated between the $\delta_{\text{iso}}$s of the two sites in $\alpha$-Na$_2$MoO$_4$.

![Fit of $^{23}\text{Na}$ MAS NMR of $\alpha$-Na$_2$MoO$_4$. The Na(1) lineshape was fit with $\delta_{\text{iso}}=-6.8$ ppm, $C_Q = 2.1$ MHz and $\eta = 1$. Na(2) was fit with $\delta_{\text{iso}} = -8.7$ ppm, $C_Q = 2.2$ MHz and $\eta = 1$.](image)

The overlap of the line shapes from two phases in the same spectrum indicates a temperature gradient within the rotor. As mentioned (chapter 3), this gradient can be as much as 50°C, although it is highly dependent on the sample size and...
properties. This temperature gradient is also responsible for the deviations in the phase transition temperatures determined for the transition to the $\alpha$-Na$_2$MoO$_4$ and melt phases, by either XRD in the literature, ($T_{XRD}$), or herein by HT NMR, ($T_{NMR}$), (Table 5.1).

5.2.2 HT $^{95}$Mo MAS NMR

$^{95}$Mo NMR is inherently very challenging to observe by NMR as it has a low receptivity, gyromagnetic ratio and natural abundance, which is further compounded by the loss of sensitivity at high temperatures from the decreased Boltzmann distribution. The acquisition of $^{95}$Mo in Na$_2$MoO$_4$ is further restricted by the relatively long relaxation times ($T_1 \geq 12s$ at room temperature), limiting the number of transients that can be acquired within the time constraints of a high-temperature NMR experiment (typically < 8 hrs).

Molybdenum in Na$_2$MoO$_4$ is at a site of tetrahedral point-group symmetry so, therefore, the $^{95}$Mo $C_Q$ is zero (Figure 5.5). With increasing temperature, the lineshape moves steadily to higher frequencies and increases in breadth up to the $\delta - \gamma$ phase transition ($500^\circ C$). At the phase-transition temperature of $500^\circ C$ the spectrum is notably narrower than the lower temperature spectra, indicating increased mobility of the $^{95}$Mo ions, averaging the SOQE. Above the phase transition temperature no NMR signal could be resolved, at least not within the experimental time frame, (acquisitions of up to 4 hrs in length were attempted in some cases).
Figure 5.5: $^{95}$Mo MAS NMR of Na$_2$MoO$_4$ as a function of temperature.
Spectra were acquired up to 675°C without producing any discernible signal, even after the acquisition of more than 6,000 transients.

It is likely that above the δ – γ phase transition (500°C) the SOQE on $^{95}$Mo increases, causing the spectrum to become broad and obscured in the noise. Although there are no structural data for γ-$\text{Na}_2\text{MoO}_4$ it may be assumed to be similar to the known β-$\text{Na}_2\text{MoO}_4$ phase, due to the similar $^{23}$Na MAS NMR and identical space group. The high-temperature β-$\text{Na}_2\text{MoO}_4$ phase has molybdenum at a site of highly distorted fourfold-coordination, (Figure 5.6).\[^8\] The average Mo–O bond lengths are also reduced to 1.521 Å, which is significant when compared to the 1.787 Å bond length in δ-$\text{Na}_2\text{MoO}_4$. It was found in chapter 4 that a decrease in M–O bond length correlates strongly with an increase in $C_Q$ for the $^{95}$Mo nucleus. By this relationship a bond length of 1.521 Å would be expected to produce a $C_Q$ on the order of 12 MHz. This is a prohibitively large $C_Q$, and the expected MAS linewidth, (equation 2.29), would be $\geq 460$ ppm which is seven times wider than the $^{95}$Mo spectrum for Na$_2$MoO$_7$ from chapter 5 which had the broadest $^{95}$Mo lineshape of the series. It is, therefore, expected that a $^{95}$Mo NMR spectrum of β-$\text{Na}_2\text{MoO}_4$ would be very challenging to acquire with the experimentation employed.

The geometry of the partially occupied molybdenum site in the α-$\text{Na}_2\text{MoO}_4$ phase is even further distorted. This site coordinates to fourteen oxygen positions with occupancies such that a distorted tetrahedral geometry is observed. The average
Figure 5.6: Mo$^{6+}$ Coordination in HT Na$_2$MoO$_4$ phases

Mo–O bond length for this phase is notably longer, 2.08 Å, but with a very high variance of bond angles (Figure 5.6). It was found that the $^{95}$Mo $C_Q$ also correlates strongly with the variance in the O-Mo-O bond length, which by this correlation would predict a $C_Q$ of $\approx 9$ MHz, which would produce an MAS linewidth of $\geq 150$ ppm. Although narrower than the expected lineshape of $\beta$–Na$_2$MoO$_4$, this is still three times larger than the $^{95}$Mo spectrum in Na$_2$Mo$_2$O$_7$.

The temperature dependence of the Mo–O bond length is due to the increased mobility of the sodium ions. As the temperature increases the sodium ions gain additional vibrational energy and will likely eventually become fully mobile. With the increased mobility the electrostatic interactions between the sodium and oxygen atoms is weakened. The oxygen atoms become increasingly attracted to the molybdenum(VI) cations as there is less electrostatic pull towards the sodium cations, resulting in shorter Mo–O bonds.

The reduction in Mo–O bond length is likely the cause of the increase in chemical
shift observed in $^{95}$Mo NMR. The centre-of-gravity shift of the $^{95}$Mo resonance increases with temperature at a rate of $0.059 \pm 0.002$ ppm/$^\circ$C. This is a significantly greater change than the $^{79}$Br resonance for KBr (-0.025 ppm/$^\circ$C), which is used for calibration of high-temperature NMR systems. It is a well established trend in oxide systems that $\delta_{iso}$ can show strong correlation with the metal-oxygen bond length, as seen for $^{23}$Na NMR in chapter 4.[27, 87] Although this trend is consistent with our high-temperature observations, it should be noted that the molybdate series studied in Chapter 4 did not show a strong $^{95}$Mo $\delta_{iso}$ correlation with Mo–O bond length. Possibly, this lack of correlation is simply due to the small data set studied in the preceding chapter, whereas a larger sampling would show a stronger trend. Conversely, it may be that the temperature dependence of the $^{95}$Mo $\delta_{iso}$ in this sample is related to the perturbation of some intrinsic NMR interaction, possibly the averaging of a large chemical shielding interaction (which is not observed under MAS conditions).

5.3 Cs$_2$MoO$_4$

Cesium is a relatively receptive nucleus with 100% natural abundance and a moderate $\gamma$, although the $T_1$'s are typically quite long. Fortunately, with increasing temperature, the $T_1$ is expected to decrease, allowing more rapid acquisition times. Cesium molybdate has an orthorhombic structure, with a single high-temperature
solid-solid phase transition at 568°C, transitioning from an orthorhombic to hexagonal crystalline phase.\textsuperscript{93} The Cs\textsubscript{2}MoO\textsubscript{4} phase near the transition temperature has been noted to be difficult to resolve by high-temperature XRD. Cs\textsubscript{2}MoO\textsubscript{4} has a melting point of 956°C.\textsuperscript{94}

5.3.1 HT \textsuperscript{133}Cs MAS NMR

At room temperature Cs\textsubscript{2}MoO\textsubscript{4} has two distinct isotropic shifts, representing the two Cs sites in the crystal structure, (Figure 5.7).\textsuperscript{7, 79} With increasing temperature up to 500°C, the two Cs\textsubscript{2}MoO\textsubscript{4} resonances shift inwards towards their average chemical shift (18 ppm) at a rate of ± 0.026 °C/ppm, (Figures 5.7, 5.8). Between 450-550°C the resonances become increasingly broad and the resolution of the two resonances becomes obscured. This is coincident with the known phase transition temperature, causing a change from the orthorhombic structure to the hexagonal high-temperature phase. The presence of broadening around the phase transition is attributed to increased disorder. This has been previously observed by XRD, where the diffraction peaks were also broadened around the phase transition temperature.
Figure 5.7: $^{133}$Cs MAS NMR of Cs$_2$MoO$_4$ as a function of temperature. CT centerbands are indicated with triangles for the low-temperature (open) and high-temperature (closed) phases.
The convergence of the two isotropic peaks is attributed to the increased mobility of the Cs\(^+\) ions with temperature, which averages the difference in chemical shielding between the two sites. Previous HT XRD analysis indicates that the single phase-transition of Cs\(_2\)MoO\(_4\) is continuous, due to the continuous temperature dependence of the unit cell parameters.\[93\] From the HT \(^{133}\)Cs MAS NMR there appears to be a strong relationship between the position of the \(^{133}\)Cs resonance of the high-temperature phase and the average position of the resonances at low-temperature, consistent with a continuous order-disorder phase transition.\[63\]

### 5.3.2 \(^{133}\)Cs NMR Dynamics

The phase change in Cs\(_2\)MoO\(_4\) can be further evidenced by observing the behaviour of the spin-lattice relaxation time. As a solid phase approaches the melting temperature the spin-lattice relaxation constant decreases at a given rate. The rate of change in \(T_1\) with increasing temperature is characteristic for a given phase, therefore differences in slope can be used to indicate phase changes.\[32, 33\] Figure 5.8b shows that at 500°C (1/\(T\times1000 = 1.29\)), where there was an observed change in the \(^{133}\)Cs MAS NMR data, (Figure 5.7), there is a distinct change in slope of log \((T_1)\), confirming this as the phase change temperature to the hexagonal phase. As per the Bloembergen, Purcell and Pound (BPP) approximation the relaxation rate is affected by the capacity for the nucleus to undergo motion.\[32, 95, 97\] As the temperature increases it is expected that the Cs\(^+\) ions become more mobile,
causing the observed decrease in $T_1$. The rate of change in $T_1$ with increasing temperature is proportional to the activation energy for motion, $E_a$ by the equation

$$T \to \infty : \ln T_1 \propto -\frac{E_a}{\kappa T}$$  \hspace{1cm} (5.1)$$

Therefore it can be concluded that above the phase change the energy barrier for movement reduces by approximately an order of magnitude, from $E_a = -8 \times 10^{-21} \text{kJ}$ to $-1 \times 10^{-19} \text{kJ}$. The change in activation energy indicates the Cs$^+$ ions are more mobile in the high temperature phase, which is consistent with the proposed change from vibrational motion of the Cs$^+$ ions in the low temperature phase to translational motion of the ions between sites.
Figure 5.8: Cs$_2$MoO$_4$ $^{133}$Cs MAS NMR temperature dependence of both $\delta_{iso}$ (a) and $\ln T_1$ (b).
5.4 Cs$_3$Na(MoO$_4$)$_2$

Cs$_3$Na(MoO$_4$)$_2$ is a crystalline phase whose composition was determined through a combination of synthesis and NMR measurements. The structure of Cs$_3$Na(MoO$_4$)$_2$ has not been determined by X-ray diffraction, but we have found circumstantial evidence suggesting it is isostructural with K$_3$Na(MoO$_4$)$_2$ (Chapter 4). Thermo-gravimetric analysis, (TGA), measurements indicate a mass loss of 5.6% between 40 and 97°C (Figure 5.9). The gradual loss of mass over this temperature range and the discontinuities in the differential thermal analysis, (DTA), signal suggest this weight loss is related to surface water. At 360 and 460°C there are inflections in the DTA signal, suggesting possible changes in the structure at these temperatures. The broad feature in the DTA signal between 500 and 650°C likely indicates some type of decomposition process. The highest temperature inflection in the DTA signal at 750°C is likely associated with the complete melting of the sample. Above 900°C there is some mass loss which may be associated with either cesium or molybdenum volatility.[66, 98]

5.4.1 HT $^{23}$Na MAS NMR

At room temperature the $^{23}$Na MAS NMR spectrum of Cs$_3$Na(MoO$_4$)$_2$ consists of a single resonance with a small $C_Q$ (730 kHz), (Figure 5.10). As the temperature is increased the $^{23}$Na lineshape narrows and the features due to the second-order quadrupolar coupling are lost. Above 210°C the lineshape is approximately
Figure 5.9: Cs$_3$Na(MoO$_4$)$_2$ DTA-TGA data acquired from room temperature to 1200°C. The mass change of 2.72 mg corresponds to a loss of approximately < 5.6%.

Lorentzian, suggesting that the sodium ions are mobile at these temperatures, averaging the broadening interactions present in ambient conditions. The sodium ions must be hopping between sodium sites at a rate faster than the magnitude of the second-order quadrupole broadening in order to account for the loss of lineshape features, in this case at a rate > 270 Hz.\textsuperscript{33}

5.4.2 HT $^{133}$Cs MAS NMR

The $^{133}$Cs MAS NMR spectrum at room temperature has two distinct sites at 161 and -144 ppm, (Figure 5.11). The large anisotropic interactions, (CSA and
Figure 5.10: $^{23}$Na MAS NMR of Cs$_3$Na(MoO$_4$)$_2$ at increasing temperatures.

$H^{(1)}_Q$, result in a multitude of spinning sidebands under MAS. With increasing temperature, the MAS rates were adjusted between 2.5 and 3.5 kHz to ensure the centerbands of the two sites did not overlap with the sidebands. As the temperature increases the two sites converge inwards similar to Cs$_2$MoO$_4$, but at a greater rate of $-0.071$ and $0.062$ ppm / °C. At 550°C a new primary resonance is present at 19 ppm. The presence of a pair of spinning sidebands for this resonance
Figure 5.11: $^{133}\text{Cs}$ MAS NMR of Cs$_3$Na(MoO$_4$)$_2$ at 9.4 T as a function of temperature. Centerbands of the low temperature phase are noted by *. The primary high temperature phase are noted by the △, with ssbs noted by the • symbols. The high temperature melt resonance is labelled with a ◊. The red line indicates the average isotropic position of the two resonances for the low temperature phase.
indicates that this resonance belongs to a new high-temperature solid phase. The resonance for the high-temperature Cs$_3$Na(MoO$_4$)$_2$ phase lies off the $\delta_{\text{avg}}$ (2 ppm ±1) for the two low-temperature resonances (Figure 5.11). This type of dissimilarity between the low-temperature and high-temperature resonances suggests the positions of the cesium ions in the two phases are unrelated, consistent with a displacive phase-transition.[63] At 575°C there is a second high-temperature site in the $^{133}$Cs NMR, at -28 ppm, which belongs to a phase with highly mobile cesium ions, as identified in the section 5.5.2.

In room temperature Cs$_3$Na(MoO$_4$)$_2$ the two $^{133}$Cs resonances have been tentatively assigned either to sites within the hexagonal unit cell, represented by the more intense resonance at 161 ppm, or sites at each corner at -144 ppm (see chapter 4). The presence of multiple phases at 575°C is consistent with the broad features in the DTA signal, implying decomposition or interactions with impurities in the sample between 500 and 700°C. It is expected that raising the temperature of the sample above 575°C would cause the resonance at -28 ppm to increase in intensity as this highly-mobile phase becomes dominant up to the melting point at 750°C melting point. Unfortunately, rotor instabilities during these experiments prevented collection above 575°C.
5.4.3 HT $^{95}$Mo MAS NMR

The $^{95}$Mo MAS NMR spectrum of Cs$_3$Na(MoO$_4$)$_2$ has a single site with a small $C_Q$ of 700 kHz at room temperature. As the temperature is increased the resonance moves towards higher frequency, at a similar rate to the $^{95}$Mo resonance in Na$_2$MoO$_4$, (Figure 5.12). There is also a moderate decrease in the peak width up to 550°C suggesting an averaging of the quadrupolar coupling with increasing temperature. The narrowing of the linewidth is consistent with the narrow resonances observed in both the $^{23}$Na and $^{133}$Cs NMR. At 550°C where the phase transition is observed in the $^{133}$Cs MAS NMR, there is an abrupt change in the width of the $^{95}$Mo resonance, consistent with the broadening typically seen in the resonances as the sample nears the phase transition. At 600°C there is a primary resonance at 22 ppm, attributed to the primary high-temperature Cs$_3$Na(MoO$_4$)$_2$ phase, noted at 19 and -14 ppm in the $^{133}$Cs NMR at 550°C. A less prominent resonance around 32 ppm is present in both the 550 and 600°C $^{95}$Mo spectra, attributed to the second HT-Cs$_3$Na(MoO$_4$)$_2$ phase, observed at -19 ppm in the $^{133}$Cs NMR. The low sensitivity of these HT $^{95}$Mo NMR spectra make further identifications and quantifications impossible.
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**Figure 5.12:** $^{95}$Mo MAS NMR of Cs$_3$Na(MoO$_4$)$_2$ as a function of temperature.
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5.5 **CsNaMoO$_4$·2H$_2$O**

TGA-DTA data for CsNaMoO$_4$·2H$_2$O were acquired up to 400°C, (Figure 5.13). Between 90 and 140°C a large mass loss of 12% was observed in the TGA, equivalent to the loss of two moles of water, confirming the identity of this crystalline phase as a dihydrate. The small increase observed in the DTA at 380-390°C was also observed in the DTA of Cs$_3$Na(MoO$_4$)$_2$ suggesting they are the same phase above 120°C.

![DTA-TGA data](image.png)

*Figure 5.13: CsNaMoO$_4$·2H$_2$O DTA-TGA data acquired up to 400°C. The mass change of 6.01 mg corresponds to a weight loss of approximately 12%.*
5.5.1 HT $^{23}$Na MAS NMR

At room temperature the $^{23}$Na MAS NMR spectrum of CsNaMoO$_4$·2H$_2$O has a single resonance with an $\eta$ of 1 (Figure 5.14). Increasing the temperature to 110°C causes a decomposition of the lineshape into multiple overlapping signals. The broader site has the same breadth and shift as Na$_2$MoO$_4$, while the narrow resonance is consistent with the presence of Cs$_3$Na(MoO$_4$)$_2$, (Figure 5.15). Integration of these two sites yields a 2:1 ratio of $^{23}$Na signal for the sites Na$_2$MoO$_4$ to Cs$_3$Na(MoO$_4$)$_2$, which corresponds to a 1:1 molar ratio of the two phases, suggesting the following reaction occurs upon dehydration of CsNaMoO$_4$·2H$_2$O:

$$3 \text{CsNaMoO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{\Delta \cdot 2\text{H}_2\text{O}} \text{Cs}_3\text{Na(MoO}_4)_2 + \text{Na}_2\text{MoO}_4$$
Figure 5.14: HT $^{23}$Na MAS NMR of CsNaMoO$_4$·2H$_2$O.
Above 500°C there is a change in the observed lineshapes, including the appearance of a new site centred at -5 ppm. At 530°C the Na$_2$MoO$_4$ lineshape becomes broader, differing from the behaviour of pure Na$_2$MoO$_4$ at this temperature. These features become even more evident at 550°C where the lineshape was fit to a $^{23}$Na $C_Q$ of 2.76 MHz, and an $\eta$ of 0, (Figure 5.16). This high-temperature resonance is always $\leq$ 60% of the total $^{23}$Na intensity, i.e., less than two-thirds of the sodium ions are in this phase. This implies that sodium ions have left this HT-Na$_2$MoO$_4$ phase to form the new high-temperature phase at -5 ppm. The $^{133}$Cs MAS NMR at this temperature indicates that the Cs$^+$ ions are in a highly mobile environment, suggesting that this change in $^{23}$Na lineshape is not associated with an incorporation of cesium. The change in this $^{23}$Na resonance from the pure Na$_2$MoO$_4$ experiments may be due to the interpenetration of the $\gamma$-Na$_2$MoO$_4$ and Cs$_3$Na(MoO$_4$)$_2$, which at elevated temperatures allows for the creation of a different HT-Na$_2$MoO$_4$ phase.

The $^{23}$Na lineshape of Cs$_3$Na(MoO$_4$)$_2$, ($\delta_{iso} = -13.3$ ppm), behaves similarly to the pure compound, except that the linewidth decreases more rapidly (Figure 5.10). The linewidths of both the Cs$_3$Na(MoO$_4$)$_2$ resonance and the resonance at -5.6 ppm are comparably narrow, suggesting both sites correspond to either liquid or highly mobile phases. The intensity of the resonance for this second phase, at $\delta_{iso} = -5.6$ ppm, grows between 530 and 550°C, at the expense of both the HT-Na$_2$MoO$_4$ and Cs$_3$Na(MoO$_4$)$_2$ resonances. The integration of the 550°C spectrum
Figure 5.15: Room temperature $^{23}$Na MAS NMR spectra at 9.4 T of: a CsNaMoO$_4$·2H$_2$O post-decomposition by HT NMR experiments, b Cs$_3$Na(MoO$_4$)$_2$ and c Na$_2$MoO$_4$. Characteristics of the lineshapes of b and c are clearly evident in the spectrum of a.
Figure 5.16: Fit of $^{23}\text{Na}$ MAS NMR of CsNaMoO$_4$·2H$_2$O at 550°C. The HT-Na$_2$MoO$_4$ phase was fit with a $\delta_{iso} = -5.5$ ppm, $C_Q = 2.76$ MHz and $\eta = 0$. The integration of the three phases, CsNaMoO$_4(l)$, Cs$_3$Na(MoO$_4$)$_2$ and HT-Na$_2$MoO$_4(s)$, was determined to be 35:28:37 (±2%), respectively.
is approximately 35:28:37 (±5%), for the melt at -5 ppm, Cs$_3$Na(MoO$_4$)$_2$ and HT-Na$_2$MoO$_4$ resonances, respectively. The molten resonance at -5 ppm grows with temperature at the cost of intensity from the other two other phases. Therefore, the phase producing this resonance must contain both Cs$^+$ and Na$^+$ ions, if the composition of the other two phases, Cs$_3$Na(MoO$_4$)$_2$ and HT-Na$_2$MoO$_4$, remain constant, suggesting it has a composition of CsNaMoO$_4$(l). The incorporation of intensity from both Cs$_3$Na(MoO$_4$)$_2$ and Na$_2$MoO$_4$ resonances into this melt resonance suggests that it will eventually become the dominant phase at very-high temperatures through the following reaction.

\[ \text{Cs}_3\text{Na(MoO}_4\text{)}_2(s) + \text{Na}_2\text{MoO}_4(s) \xrightarrow{\Delta} 3\text{CsNaMoO}_4(l) \]

### 5.5.2 HT $^{133}$Cs MAS NMR

At room temperature the $^{133}$Cs MAS NMR spectrum of CsNaMoO$_4$·2H$_2$O has a single isotropic peak at -70 ppm with many spinning sidebands, (Figure 5.17). This resonance appears insensitive to temperature up to 100$^\circ$C. Above 100$^\circ$C, a transformation occurs in the sample. After remaining at 120$^\circ$C for approximately 10-20 minutes, the only $^{133}$Cs peaks present in the sample are at 148 and -130 ppm and associated ssbs identical to the positions of the two sites in Cs$_3$Na(MoO$_4$)$_2$ at this temperature. Upon further heating the two peaks converge at an identical temperature dependent rate as that found for pure Cs$_3$Na(MoO$_4$)$_2$. At 500$^\circ$C
Figure 5.17: HT $^{133}$Cs MAS NMR of CsNaMoO$_4$·2H$_2$O. Isotropic resonances are indicated with *. The top spectrum was acquired after the highest temperature spectrum was completed and the system was cooled back to room temperature.
a new and relatively broad resonance is observed, centred at -27 ppm, this differs from the primary high-temperature phase observed in pure Cs$_3$Na(MoO$_4$)$_2$ (19 ppm). At 550°C the two $^{133}$Cs peaks of the LT-Cs$_3$Na(MoO$_4$)$_2$ phase are no longer observed and the resonance at -27 ppm has resolved as two narrower lines at -28 (30% relative intensity) and -31 ppm (60%). The narrow breadths of the two sites and lack of spinning sidebands suggest that both resonances belong to phases with highly mobile cesium cations. The observation of two narrow resonances in the $^{133}$Cs MAS NMR is consistent with the two narrow sites in the $^{23}$Na MAS NMR. The lower intensity site (-28 ppm) was previously observed as a minor resonance in the high-temperature $^{133}$Cs MAS NMR experiments of Cs$_3$Na(MoO$_4$)$_2$, as mentioned above. The second, higher intensity, $^{133}$Cs site (-31 ppm) is attributed to the CsNaMoO$_4$(l) phase identified in the $^{23}$Na NMR at 575°C (section 5.5.1). The composition of the high-temperature melt phase can be shown to be CsNaMoO$_4$(l) by considering the integrations of both the $^{133}$Cs and $^{23}$Na MAS NMR data. From the integration of the $^{133}$Cs MAS NMR data at 550°C it is found that the intensity is in a 1:2 ratio for the two phases, while the $^{23}$Na MAS NMR suggests that sodium is in a 5:4 ratio, for the CsNaMoO$_4$(l) and Cs$_3$Na(MoO$_4$)$_2$ phases, respectively. Considering only the ratios of intensities for the narrow resonances, while assuming that one phase is a HT-Cs$_3$Na(MoO$_4$)$_2$ phase, the other high-temperature phase can be estimated to have a composition with a near 1:1 ratio of Cs:Na (1.09:0.91 ±0.05), confirming its composition as CsNaMoO$_4$(l).
5.5.3 HT $^{95}$Mo MAS NMR

$^{95}$Mo MAS NMR also shows the decomposition from a single CsNaMoO$_4$·2H$_2$O peak into the two resonances of Cs$_3$Na(MoO$_4$)$_2$ and Na$_2$MoO$_4$ above 100°C, (Figure 5.18). These temperature-dependent peaks shift at identical rates, which are consistent with the pure samples. At 550°C, two peaks are observed, one at 32 ppm (56% relative intensity) and another at 22 ppm (44%). The higher frequency site is not observed in either the 550°C $^{95}$Mo spectrum of Na$_2$MoO$_4$ or Cs$_3$Na(MoO$_4$)$_2$. This resonance at 32 ppm is attributed to the putative CsNaMoO$_4$($l$) phase observed in the $^{23}$Na (at -5 ppm) and $^{133}$Cs (at -31 ppm) MAS NMR at 550°C. The site at 22 ppm in the $^{95}$Mo MAS NMR is consistent with the expected Cs$_3$Na(MoO$_4$)$_2$ phase, observed in the $^{23}$Na and $^{133}$Cs NMR of the pure compound, (Figure 5.19). The two sites observed at 550°C have an integrated intensity of 45:55, for CsNaMoO$_4$($l$):Cs$_3$Na(MoO$_4$)$_2$. This ratio is within error of the expected ratio predicted from either the $^{23}$Na or $^{133}$Cs MAS NMR data, both of which predict a 40:60 (±5) integration in the $^{95}$Mo NMR. It is expected that the resonance for the remaining Na$_2$MoO$_4$(s) observed in the $^{23}$Na NMR at this temperature will have too large a $C_Q$ to be observed.

5.5.4 Discussion of CsNaMoO$_4$·2H$_2$O results

Increasing the temperature of CsNaMoO$_4$·2H$_2$O to 550°C produces a mixture of three phases, Na$_2$MoO$_4$(s), Cs$_3$Na(MoO$_4$)$_2$ and CsNaMoO$_4$($l$), as observed by the
Figure 5.18: HT $^{95}$Mo MAS NMR of CsNaMoO$_4$·2H$_2$O. a. Sample at 21°C after high-temperature experiments, b. Sample at 550°C, c. Sample at 300°C, d. Spectrum of CsNaMoO$_4$·2H$_2$O sample before high-temperature experiments. ○ symbols indicate peaks associated with Na$_2$MoO$_4$, this phase is not evident at 550°C. ◇ symbols indicate $^{95}$Mo resonance of Cs$_3$Na$_4$(MoO$_4$)$_2$. ▽ indicates the CsNaMoO$_4$($l$) resonance.
Figure 5.19: HT $^{95}$Mo MAS NMR of a. Na$_2$MoO$_4$, b. Cs$_3$Na(MoO$_4$)$_2$ and c. CsNaMoO$_4$·2H$_2$O at 550°C.
combination of $^{23}\text{Na}$, $^{133}\text{Cs}$ and $^{95}\text{Mo}$ MAS NMR. It is predicted that as the sample is increased past the observable temperature range, the molten CsNaMoO$_4$ peaks will become the dominant phase, implying a re-convergence of the sample into a single phase at very high temperatures. Unfortunately, our experimental setup would be at risk of failure under these conditions, since the system requires continuous MAS, which cannot be sustained with a liquid sample. Both a near-molten Cs$_3$Na(MoO$_4$)$_2$ phase and CsNaMoO$_4(l)$ exist simultaneously at these temperatures, but upon cooling, only Cs$_3$Na(MoO$_4$)$_2(s)$ and Na$_2$MoO$_4(s)$ are observed. Therefore, upon cooling CsNaMoO$_4(l)$ appears to undergo a disproportionation reaction, forming Cs$_3$Na(MoO$_4$)$_2(s)$ and Na$_2$MoO$_4(s)$. It is expected that upon cooling CsNaMoO$_4(l)$ from temperatures $> 550^\circ\text{C}$ the two phases Cs$_3$Na(MoO$_4$)$_2(s)$ and Na$_2$MoO$_4(s)$ will be interpenetrated.

It is plausible that the production of Cs$_3$Na(MoO$_4$)$_2(s)$ and Na$_2$MoO$_4(s)$ from the decomposition of CsNaMoO$_4\cdot 2\text{H}_2\text{O}$ produces a nanocrystalline mixture. When the crystallite sizes become sufficiently small the melting point can decrease dramatically.\[99\] This effect can be aggravated in a nanocrystalline mixture of phases with different unit cells and crystallite sizes.\[100, 101\] This “flux” formed upon the mixing of these possibly nanocrystalline phases explains the greater intensity of the melt phases found in the CsNaMoO$_4\cdot 2\text{H}_2\text{O}$ experiments at 550$^\circ\text{C}$ relative to the Cs$_3$Na(MoO$_4$)$_2$ experiments.
5.6 Conclusions

The temperature dependence of Na$_2$MoO$_4$ and Cs$_2$MoO$_4$ has been well characterized by high-temperature NMR, showing consistent results with the data from the literature. Cs$_2$MoO$_4$ has a single phase transition that can be easily followed through observation of changes in the $^{133}$Cs $\delta_{iso}$. The sensitivity, temperature dependence of $\delta_{iso}$ and the predictable $T_1$ behaviour of $^{133}$Cs MAS NMR of Cs$_2$MoO$_4$ makes it a suitable candidate for temperature calibration. The breadths and complexity of the $^{23}$Na MAS NMR lineshapes of Na$_2$MoO$_4$ make high-temperature studies more challenging. The mixed cation salts, Cs$_3$Na(MoO$_4$)$_2$ and CsNaMoO$_4$$\cdot$2H$_2$O, undergo considerably more complex high-temperature chemistry than either of the single cation salts. Cs$_3$Na(MoO$_4$)$_2$ shows similar behaviour to Cs$_2$MoO$_4$, with the presence of two temperature-dependent resonance, which converge upon heating. The single solid-solid phase transition in Cs$_3$Na(MoO$_4$)$_2$ results in multiple high-temperature resonances, which suggests it is not a direct disorder-order transition as in Cs$_2$MoO$_4$. The decomposition of CsNaMoO$_4$$\cdot$2H$_2$O upon dehydration into Cs$_3$Na(MoO$_4$)$_2$ and Na$_2$MoO$_4$ was observed by high-temperature $^{23}$Na MAS NMR. Upon further heating of this mixture two molten phases become evident in both $^{23}$Na and $^{133}$Cs NMR at 550°C. This pair of molten or highly-mobile phases was identified as Cs$_3$Na(MoO$_4$)$_2$ and CsNaMoO$_4$(l), which, upon cooling produce two interpenetrating crystalline phases, Cs$_3$Na(MoO$_4$)$_2$(s) and Na$_2$MoO$_4$(s).
Chapter 6

High Temperature MAS NMR of Model Nuclear Waste Systems.

Nuclear waste storage glasses are complex materials made of many components (≥ 20 elements). In addition to their compositional complexity, these materials can separate into multiple phases which can be either crystalline or vitreous. To study the origins of this phase separation, high-temperature MAS NMR experiments were performed on a series of model nuclear waste materials. Three glasses, (CM3, CM5 and CM10), were synthesized with differing amounts of cesium and molybdenum. The synthesis of these glasses is described in chapter 3. Table 6.1 repeats the Cs, Na and Mo concentrations for reference. Samples were prepared with 1.5x times the target Cs₂O content in order to allow for cesium volatilization;
this procedure was determined from our lab’s extensive experience synthesizing cesium-bearing glasses.\[66\]

### 6.1 Design

Both Cs and Mo were increased with respect to the other oxides to encourage crystalline phase separation, while also making the glasses more suitable for investigations by $^{133}$Cs MAS NMR. Even at 10\% MoO$_3$ there is not sufficient $^{95}$Mo in the samples for detection by HT MAS NMR within the restricted time frames of these experiments. The three glasses were made at 1300$^\circ$C and vitrified by either quenching (CM3) or slow cooling (CM5 and CM10). By quenching CM3 and using minimal amounts of Cs and Mo, the crystallinity was minimized. CM5 and CM10 glasses were slow cooled to encourage crystallization, emphasizing any possible interactions between the crystalline phases and the bulk glass at high temperatures.

**Table 6.1:** Concentrations of cesium, sodium and molybdenum in CMx glass series.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>CM3</th>
<th>CM5</th>
<th>CM10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$O (mol%)</td>
<td>3</td>
<td>5.2</td>
<td>10.4</td>
</tr>
<tr>
<td>MoO$_3$ (mol%)</td>
<td>2.5</td>
<td>5.2</td>
<td>10.4</td>
</tr>
<tr>
<td>Na$_2$O (mol%)</td>
<td>16</td>
<td>9.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

### 6.2 Methods

$^{23}\text{Na}$ and $^{133}\text{Cs}$ MAS NMR experiments were performed on the three glasses at both 14.1 T and 9.4 T. At 14.1 T a 1.6 mm veryFast MAS probe was used, allowing for MAS rates of 30 kHz and ensuring complete separation of the central transition centerband from the spinning sideband manifold. At 9.4 T the high-temperature 7mm MAS probe was employed, using applied MAS rates of 2.5 to 3.5 kHz.

### 6.3 Room Temperature NMR

The room-temperature $^{23}\text{Na}$ and $^{133}\text{Cs}$ NMR spectra for the three glasses were collected at 14.1 T and 30 kHz MAS. These conditions provide improved sensitivity and resolution with respect to the lower field (9.4 T) and slower spinning (3 kHz) spectra collected with the high-temperature system. Figure 6.1 shows the effect of the lower spinning rate and field on the separation and resolution of multiple $^{23}\text{Na}$ NMR resonances. For $^{133}\text{Cs}$ MAS NMR the effect is even more extreme due to the much broader glass resonances, (widths of $\geq$ 100 ppm at 14.1 T (Figure 6.3) vs $\approx$15 ppm for $^{23}\text{Na}$ glass resonances), which have equally broadened spinning sidebands. At 9.4 T and 3 kHz MAS, the $^{133}\text{Cs}$ NMR glass signal is dispersed sufficiently that the glass resonance is difficult to differentiate from the baseline.

To mimic repository conditions the glasses were stored in conditions of ambient humidity and in an air atmosphere. Under these conditions the crystalline phases
Figure 6.1: Example fit of $^{23}$Na MAS NMR of CM5 glass; the 9.4 T data were collected at 3 kHz MAS, while the 14.1 T data were acquired at 30 kHz. Note that at 9.4 T there is a multitude of spinning sidebands overlapped with the centerband, while at 14.1 T the spinning sidebands are outside the displayed spectral window.

$^{23}$Na MAS NMR (figure 6.2) shows the formation of CsNaMoO$_4$·2H$_2$O at $\delta_{\text{iso}} = 0.5$ ppm, in all samples. $^{133}$Cs MAS NMR (figure 6.3) confirms the presence of CsNaMoO$_4$·2H$_2$O, $(\delta_{\text{iso}} = -70$ ppm). Upon fitting the spectra of CM3 and CM5 glasses there was evidence of Na$_2$MoO$_4$ and Na$_2$MoO$_4$·2H$_2$O phases, comprising 3 and 5% of the $^{23}$Na intensity, respectively (see example fit in figure 6.1). The $^{23}$Na glass resonance is distinctly non-Gaussian, which is common in spectra of
quadrupolar nuclei in disordered environments.\cite{65,102} This characteristic lineshape is due to the presence of a distribution of chemical shifts and a significant variation of EFG tensors across the collection of spins. A Czjzek distribution was used to fit this glass site, which has been successfully applied in many examples of disordered quadrupoles.\cite{102,103} The $\delta_{\text{iso}}$ for the glass resonance in both $^{133}$Cs and $^{23}$Na NMR of the CM5 and CM10 samples is shifted to lower frequency compared to the CM3 sample.

The $^{23}$Na MAS NMR data at 14.1 T were fit with the known lineshapes for CsNaMoO$_4$·2H$_2$O and Na$_2$MoO$_4$ or Na$_2$MoO$_4$·2H$_2$O, as well as a Czjzek distribution estimating the glass portion. Using these assignments the integrated intensities for the various phases was determined (Table 6.2). The $^{133}$Cs MAS NMR spectra at 14.1 T were fitted with a broad Gaussian distribution representing the glass and a narrow peak at $\delta_{\text{iso}} = -70$ ppm representing CsNaMoO$_4$·2H$_2$O. In CM10 a $^{133}$Cs resonance at -44 ppm was tentatively assigned as the $\delta_{\text{iso}}$ of Cs$_2$Mo$_3$O$_{10}$, with an integrated intensity of 1%.\cite{104} The two resonance accounting for 1% of the $^{133}$Cs intensity in CM5 were unidentified, while the five unknown resonances in CM10 contained 7% of the total cesium intensity. These resonances are likely either uncharacterized cesium molybdates, or cesium silicates. Cesium silicates have been shown to have a range of $^{133}$Cs chemical shifts spread between 70 and -15 ppm.\cite{105}
Figure 6.2: $^{23}$Na MAS NMR at 14.1 T of cesium- and molybdenum-enriched model waste storage materials.
Figure 6.3: $^{133}$Cs MAS NMR at 14.1 T of cesium- and molybdenum-enriched glasses. Spectra for CM5 and CM10 are scaled outside of their bounding boxes to visualize the lower intensity resonances.

From the integrated intensity an estimate of the amount of molybdenum in crystalline phases can be made (Table 6.2). For this estimation the amount of cesium and sodium in crystalline phases was interpreted directly from the intensity of the sites in their respective NMR spectra and normalized by their expected concentration in each sample. The amount of Mo in molybdenum-bearing crystalline phases was found by assuming the unknown phases in the $^{133}$Cs MAS NMR spectra had an equivalent composition of $\text{Cs}_2\text{MoO}_4$. This can only be used to form a tentative
### Table 6.2: Interpretation of sample composition from 14.1 T MAS NMR data

<table>
<thead>
<tr>
<th>Sample</th>
<th>CM3</th>
<th>CM5</th>
<th>CM10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{23}$Na MAS NMR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass $\delta_{iso}$ (± 0.5) ppm</td>
<td>3.2</td>
<td>-9.0</td>
<td>-9.0</td>
</tr>
<tr>
<td>$^{133}$Cs MAS NMR</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass $\delta_{iso}$ (± 2) ppm</td>
<td>22</td>
<td>-21</td>
<td>-17</td>
</tr>
<tr>
<td>% of $\text{Na}^+$ in $\text{CsNaMoO}_4\cdot2\text{H}_2\text{O}$ (± 0.5)$^a$</td>
<td>3</td>
<td>1</td>
<td>24</td>
</tr>
<tr>
<td>% of $\text{Na}^+$ in $\text{Na}_2\text{MoO}_4$ (± 0.5)$^a$</td>
<td>3</td>
<td>5.0(hydrate)</td>
<td>0</td>
</tr>
<tr>
<td>% of $\text{Cs}^+$ in $\text{CsNaMoO}_4\cdot2\text{H}_2\text{O}$ (± 0.5)$^b$</td>
<td>2</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>% of $\text{Cs}^+$ in $\text{Cs}_2\text{Mo}<em>3\text{O}</em>{10}$ (± 0.5)$^b$</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>% of $\text{Cs}^+$ in unknown (± 0.5)$^b$</td>
<td>0</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>% of $\text{Mo}^{6+}$ in crystalline phases$^c$</td>
<td>44-45</td>
<td>53 - 57</td>
<td>43-59</td>
</tr>
<tr>
<td>$R = \frac{\text{Cs}<em>2\text{O}</em>{\text{glass}}+\text{Na}<em>2\text{O}</em>{\text{glass}}}{\text{B}_2\text{O}_3}$</td>
<td>1.1</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>$K = \frac{\text{Si}_2\text{O}_5+\text{MoO}_3}{\text{B}_2\text{O}_3}$</td>
<td>3.9</td>
<td>4.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Minimum % crystallinity$^d$</td>
<td>2 ± 0.1</td>
<td>2 ± 0.2</td>
<td>8 ± 1</td>
</tr>
</tbody>
</table>

$^a$ With respect to total Na content.

$^b$ With respect to total Cs content.

$^c$ With respect to total Mo content.

$^d$ Estimated from the total number of cations in crystalline phases with respect to the total composition.

estimate for the amount of molybdenum retained in the glass, due to the possibility of higher-order cesium molybdates or cesium silicates in the samples. These estimates were used to approximate the composition of the glass, as represented by $R$, $K$ and the % of minimum crystallinity. $R$ is used to describe the ratio of glass modifiers, ($\text{Cs}_2\text{O}_{\text{glass}}$ and $\text{Na}_2\text{O}_{\text{glass}}$), to boron content.

$$R = \frac{\text{Cs}_2\text{O}_{\text{glass}} + \text{Na}_2\text{O}_{\text{glass}}}{\text{B}_2\text{O}_3}$$  \hspace{1cm} (6.1)
While $K$ describes the ratio of $\text{SiO}_2$ and $\text{MoO}_3\text{glass}$ to $\text{B}_2\text{O}_3$.

$$K = \frac{\text{SiO}_2 + \text{MoO}_3\text{glass}}{\text{B}_2\text{O}_3} \quad (6.2)$$

These ratios give an indication of the relative connectivity of the glass network across the series.

### 6.4 High-Temperature MAS NMR of Model Nuclear Waste Materials

$^{23}\text{Na}$ and $^{133}\text{Cs}$ HT MAS NMR experiments were performed at 9.4 T for the three samples at temperatures up to $650^\circ\text{C}$.

#### 6.4.1 $^{23}\text{Na}$ MAS NMR of CM10

The room temperature $^{23}\text{Na}$ MAS NMR results for CM10 at 9.4 T show evidence of two distinct sodium environments (Figure 6.4), consistent with the 14.1 T data (Figure 6.2). The $^{23}\text{Na}$ MAS NMR spectrum consists of a broad glass resonance overlapped by the broad second-order quadrupole lineshape of CsNaMoO$_4 \cdot 2\text{H}_2\text{O}$, distinguished by the peak maximum at -5 ppm, (Figure 6.4). The 14.1 T data indicates that 24% of the Na$^+$ ions are located in this crystalline phase (Table 6.2). Upon heating, the CsNaMoO$_4 \cdot 2\text{H}_2\text{O}$ phase is retained up to 150$^\circ\text{C}$. At and
above 200°C the narrow resonance of Cs$_3$Na(MoO$_4$)$_2$ (centred at -13 ppm) becomes a dominant spectral feature. Due to the proposed decomposition mechanism of CsNaMoO$_4$·2H$_2$O (see chapter 5) Na$_2$MoO$_4$ is expected to be present in the sample upon dehydration, but its lineshape is convoluted with the broad glass resonance. At 500°C a new resonance at -5 ppm is present, consistent with the CsNaMoO$_4$(l) phase observed in the HT $^{23}$Na MAS NMR trials for CsNaMoO$_4$·2H$_2$O. (See section 5.5). As the sample is cooled, the CsNaMoO$_4$(l) phase remains present down to 400°C, increasing in breadth with decreasing temperature. The Cs$_3$Na(MoO$_4$)$_2$ crystalline phase becomes reduced with the introduction of the CsNaMoO$_4$(l) phase at 500°C, but becomes a dominant feature upon cooling to 300°C. The room temperature spectrum recorded after cooling has a similar lineshape to the spectrum at 200°C, suggesting the total sample crystallinity has not been altered by the high-temperature experiments.
Figure 6.4: HT $^{23}$Na MAS NMR of CM10, a phase-separated model nuclear waste material. ▽ indicates the peak maximum for CsNaMoO$_4$·2H$_2$O. ○ indicates the maximum for Cs$_3$Na(MoO$_4$)$_2$. ◁ indicates CsNaMoO$_4$($l$). □ indicates the high-frequency edge of the Na$_2$MoO$_4$ lineshape.
6.4.2 $^{133}$Cs MAS NMR of CM10

At room temperature and 9.4 T the $^{133}$Cs MAS NMR of CM10 consists of a spinning sideband manifold centred at -70 ppm, consistent with CsNaMoO$_4$·2H$_2$O, (Figure 6.5). The second spectrum collected was at 300°C, taking advantage of the reduced relaxation delays (5s vs 120s at 21°C), allowing for more rapid collection times. The spectrum is convoluted due to the overlap of the many spinning sidebands for the two sites in Cs$_3$Na(MoO$_4$)$_2$, the resonance at -44 ppm of Cs$_2$Mo$_3$O$_{10}$, and the five unknown resonances identified in the 14.1 T data, (Figure 6.3). The glass peak for these experiments is quite broad, over 100 ppm at 14.1 T. Additionally, at 14.1 T and 30 kHz MAS, third- and fourth-order spinning sidebands were visible in the spectra, suggesting significant first order interactions for these sites. Therefore, at 9.4 T and one-tenth the MAS rate used at 14.1 T the broad glass resonance will be completely convoluted with its equally broad spinning sidebands, spreading the total $^{133}$Cs signal over a large frequency range. This prevents the resolution of the glass signal from the baseline in these high-temperature spectra.

At 500°C the spectrum is drastically different, consisting of two new resonances at -45 ppm and -48 ppm, with integrated intensities of 31 and 69%, respectively, (table 6.3). This is consistent with the observed change in the $^{23}$Na MAS NMR of this sample at 500°C. A similar spectrum was acquired for CsNaMoO$_4$·2H$_2$O at 550°C, with $^{133}$Cs resonance at -28 and -31 ppm, in a ratio of 1:2, respectively,
Figure 6.5: HT $^{133}$Cs MAS NMR of CM10 model waste material at 9.4 T. The spectra collected between 300°C and 500°C are not shown due to their poor signal-to-noise, in addition to being convoluted by the overlap of the seven possible resonances and their spinning sidebands. △ indicates $\delta_{\text{iso}}$ of CsNaMoO$_4$·2H$_2$O. ○ indicates $\delta_{\text{iso}}$ for the sites in Cs$_3$Na(MoO$_4$)$_2$. ● indicate several prominent spinning sidebands of Cs$_3$Na(MoO$_4$)$_2$ that could be identified. ◁ indicate the high-temperature resonances (CsNaMoO$_4$(l), and Cs$_3$Na(MoO$_4$)$_2$).
(Figure 5.17). The two resonances observed at 500°C converge into a single resonance upon cooling to 450°C. Upon cooling to 300°C, the spectrum still contains a broad feature centred at -47 ppm, as well as evidence of Cs₃Na(MoO₄)₂(s) and two unknown resonances at 14 and -22 ppm, (Figure 6.5). The high-temperature peaks remain the only resonances upon cooling down to 300°C, where the peaks for Cs₃Na(MoO₄)₂ (156 ppm) and two additional phases, (14 and -20 ppm) become visible. The high-temperature phase is no longer evident upon cooling below 300°C. The samples were not recoverable after the HT NMR experiments, due to the fusion of the sample lids caused by the presence of the melted sample. Consequently, these heat-treated samples could not be studied at higher field and spinning rates.

6.4.3 ²³Na MAS NMR of CM5

At room temperature the 14.1 T ²³Na MAS NMR spectrum for sample CM5 show that the ions are dispersed amongst the CsNaMoO₄·2H₂O (1%), Na₂MoO₄·2H₂O (5%) and glass (94%) phases (Table 6.2). At 9.4 T, the ²³Na MAS NMR spectrum shows evidence of CsNaMoO₄·2H₂O by the characteristic inflection at -5 ppm, but the Na₂MoO₄·2H₂O lineshape is convoluted with the glass resonance, as demonstrated in Figure 6.1. Upon heating the sample, the CsNaMoO₄·2H₂O resonance is visible up to 150°C, above this temperature the Cs₃Na(MoO₄)₂ peak is visibly overlapped with the glass resonance (Figure 6.6). At 600 and 650°C a narrow peak
appears at -5 ppm, consistent with CsNaMoO$_4$(l) phase mentioned previously. A second inflection is seen at -12.5 ppm, consistent with the expected Cs$_3$Na(MoO$_4$)$_2$ phase, (Table 6.3). The high temperature phase is still observed upon cooling to 550°C, although its contribution to the overall lineshape is reduced. At room temperature the lineshape appears to show evidence of both Cs$_3$Na(MoO$_4$)$_2$ and Na$_2$MoO$_4$ resonances, although convoluted with the bulk glass phase.
Figure 6.6: HT $^{23}$Na MAS NMR at 9.4 T and 3 kHz MAS of CM5, a phase-separated model nuclear waste material. ▽ indicates the peak maximum for CsNaMoO$_4$·2H$_2$O. ○ indicates the maximum for Cs$_3$Na(MoO$_4$)$_2$. ◀ indicates CsNaMoO$_4$(l). ◇ indicates the high-frequency edge of the Na$_2$MoO$_4$ lineshape.
6.4.4 $^{133}$Cs MAS NMR of CM5

Because $^{133}$Cs MAS NMR of the CM5 material has very poor signal-to-noise ratio at 9.4 T and 3 kHz MAS, the low temperature ($< 500^\circ$C) spectra were inconclusive (not shown). This is due to a combination of low crystallinity in the sample and the division of the signal into many spinning sidebands. The crystallinity was estimated from the 14.1 T data, showing $^{133}$Cs ions in 2.3% CsNaMoO$_4$·2H$_2$O, 96.5% glass and 1.2% in unknown phases (Figure 6.3). At 500$^\circ$C a narrow resonance centered at -42 ppm is observed (Figure 6.7). This peak appears to be the sum of two overlapped resonances at -43 and -40 ppm, integrating to 74 and 26%, respectively. This ratio and the relative chemical shifts are consistent with the phases observed in the $^{133}$Cs MAS NMR of both CM10 and CsNaMoO$_4$·2H$_2$O (section 5.5.2), at similar temperatures (500 and 550$^\circ$C). The observation of this melt peak is consistent with the presence of a narrow resonance in the $^{23}$Na NMR of CM5 above 500$^\circ$C.
Figure 6.7: HT $^{133}$Cs MAS NMR of CM5, a phase-separated model nuclear waste material. Spectra below 500°C did not have sufficient signal-to-noise for analysis.

6.4.5 $^{23}$Na MAS NMR of CM3

At room temperature the $^{23}$Na MAS NMR spectrum at 14.1 T indicates that CsNaMoO$_4$·2H$_2$O and Na$_2$MoO$_4$ are the major crystalline phases. The Na$_2$MoO$_4$ and CsNaMoO$_4$·2H$_2$O phases only contribute to 5.5% of the total $^{23}$Na intensity, and are therefore not visible in the room temperature spectrum acquired at 9.4 T and 3 kHz MAS. As the sample is heated to 300°C, an inflection in the broad
glass resonance appears at \( \approx -10 \) ppm, consistent with expected transformation of CsNaMoO\(_4\)·2H\(_2\)O to Cs\(_3\)Na(MoO\(_4\))\(_2\) (Figure 6.8). At 400 and 500\(^\circ\)C a peak at -5 ppm becomes evident, consistent with the CsNaMoO\(_4\)(\(l\)) phase observed in the other materials. Additionally a small inflection at -12.6 ppm is present, likely indicating the presence of highly mobile Cs\(_3\)Na(MoO\(_4\))\(_2\), (Table 6.3).

**Table 6.3:** Observed chemical shifts of high temperature phases

<table>
<thead>
<tr>
<th>Sample</th>
<th>CM3 (\delta_{\text{CGS}}) ppm</th>
<th>CM5 (\delta_{\text{CGS}}) ppm</th>
<th>CM10 (\delta_{\text{CGS}}) ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{23}\text{Na MAS NMR})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsNaMo((l))</td>
<td>-5.6 ppm 6</td>
<td>-7.1 ppm 9</td>
<td>-7.1 ppm 20</td>
</tr>
<tr>
<td>Cs(_3)Na(MoO(_4))(_2)</td>
<td>-12.6 ppm 1</td>
<td>-12.5 ppm 2</td>
<td>-12.9 ppm 3</td>
</tr>
<tr>
<td>Glass</td>
<td>-26.5 ppm 93</td>
<td>-27.7 ppm 89</td>
<td>-20.0 ppm 77</td>
</tr>
<tr>
<td>Temperature</td>
<td>500(^\circ)C</td>
<td>600(^\circ)C</td>
<td>500(^\circ)C</td>
</tr>
<tr>
<td>(^{133}\text{Cs MAS NMR})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsNaMo((l))</td>
<td>-32 ppm 100</td>
<td>-43 ppm 74</td>
<td>-48 ppm 69</td>
</tr>
<tr>
<td>Cs(_3)Na(MoO(_4))(_2)</td>
<td>– –</td>
<td>-40 ppm 26</td>
<td>-45 ppm 31</td>
</tr>
<tr>
<td>Temperature</td>
<td>550(^\circ)C</td>
<td>500(^\circ)C</td>
<td>500(^\circ)C</td>
</tr>
</tbody>
</table>
Figure 6.8: HT $^{23}\text{Na}$ MAS NMR of CM3, a phase-separated model nuclear waste material. ○ indicates the maximum for $\text{Cs}_3\text{Na}($MoO$_4)_2$. ◊ indicates $\text{CsNaMoO}_4(l)$. 
6.4.6 $^{133}$Cs MAS NMR of CM3

The $^{133}$Cs MAS NMR was very challenging for this sample due to the low cesium content (3%). From the 14.1 T data the cesium ions are found to be in either the CsNaMoO$_4$·2H$_2$O (2%) phase or in the bulk glass. Upon heating to 550°C a single narrow resonance is observed at -32 ppm, (Figure 6.9). This high-temperature resonance has a much shorter relaxation time, allowing for the collection of many scans within the time constraints of the high-temperature experiment. Even with a large set of transients the signal-to-noise ratio is still relatively poor.

![Figure 6.9: HT $^{133}$Cs MAS NMR of CM3, a phase separated model nuclear waste material. The sample does not have sufficient sensitivity below 550°C for $^{133}$Cs MAS NMR.](image-url)
6.5 Discussion

As the molybdenum content increases from 2.5 mol% to 5 mol% there is only a small increase in the overall crystallinity in the sample. Upon doubling the molybdenum content from 5 to 10 mol% there is a four-fold increase in crystallinity, suggesting there is a maximum threshold for this glass composition to retain molybdenum within the vitreous network (table 6.3,[106, 107]).

The CM3 glass was made using a different ratio of Cs:Na:Mo than CM5 and CM10; approximately 20% more cesium and sodium was used in the latter glasses. This change in Cs and Na content affects the bulk glass structure, as can be seen by the decrease in $R$ between CM3 and CM5 (Equation 6.1, Table 6.2). The smaller change in $R$ between CM5 and CM10 is caused primarily by greater devitrification in the latter, removing Cs and Na ions from the glass network. The change in the chemical shift of the $^{23}$Na and $^{133}$Cs glass resonances to lower frequency with decreasing $R$ has been characterized previously in the literature.[27] This change in chemical shift is attributed to a decrease in the coordination sphere for these cations as the ratio of glass modifiers to glass formers decreases.

6.5.1 Comparison of HT $^{23}$Na MAS NMR

Upon heating the various glasses there is a characteristic high-temperature phase that grows in the $^{23}$Na MAS NMR at or above 500°C. This phase appears between
-5 and -8 ppm, consistent with the high-temperature CsNaMoO$_4$(l) phase identified in the CsNaMoO$_4$·2H$_2$O trials in chapter 5. Additionally, there is a minor amount of Cs$_3$Na(MoO$_4$)$_2$ present in each glass, typically accounting for between 10 and 20% of the total devitrification in the sample. The resonances show little change in position between samples, appearing to be compositionally insensitive. The total intensity of the high-temperature phase agrees within error with the initial crystallinity found at room temperature, suggesting that there is no mixing between the sodium ions in crystalline phases and those in the bulk glass.

There appears to be some variance in the temperature that the high-temperature CsNaMoO$_4$(l) phase becomes evident between compositions. Both CM10 and CM3 showed evidence of the high temperature phase forming at 500°C, while CM5 shows a higher phase-transition temperature (600°C). Notably, in all but the CM5 case, the melt phase is observed at lower temperatures than is observed for pure CsNaMoO$_4$·2H$_2$O (550°C) (Figure 6.10). This deviation in phase-transition temperature is likely related to a difference in the crystallite size within the materials. The melting point of nanocrystalline phases interpenetrated in a glass matrix has been shown to have a direct dependence on crystallite size, with decreases of upwards of 200°C having been observed in highly nanocrystalline phases. The different transition temperatures recorded for the CM5 sample and CM3 samples show the effect of different cooling rates, with CM3 being quenched and CM5 being slow-cooled, allowing larger crystallites to form. CM10 also has a lower phase transition point than CM5 but it is formed from the coalescence of many more
phases than the other glasses (eight crystalline distinct resonances were determined in the fit of the $^{133}$Cs MAS NMR). It has also been shown that a multiphase polycrystalline mixture can also result in lower overall melting points than any one pure phase, possibly causing the lower transition point in CM10.\footnote{21}

These deviations in phase transition temperatures between the solid and liquid also appear to impact the liquid-to-solid transition upon cooling. In the CM5 glass, which has the highest transition temperature, the liquid phase returns to solid at only 550°C. Comparably, CM10 retains the high-temperature phases well into the region of 300-400°C upon cooling, as observed via the combination of $^{133}$Cs and $^{23}$Na MAS NMR. The broadening of the high-temperature resonances with cooling suggests decreased motion, indicating that the phases are increasing in viscosity. Although the primary mechanism for these deviations is likely the cooling rates, the size of the crystalline phase inclusions within the glass may also play a role. Smaller inclusions will reduce the effective melting point of the crystalline phases, allowing these phases to remain present at lower temperatures.
Figure 6.10: Comparison of HT $^{23}$Na MAS NMR of phase-separated model waste samples (CMx) and pure crystal phase of CsNaMoO$_4$·2H$_2$O studied in chapter 5.
6.5.2 Comparison of HT $^{133}$Cs MAS NMR

Each of the spectra has narrow resonances above 500 or 550°C. The observed chemical shifts appear to be compositionally dependent, appearing between -30 to -50 ppm, (Figure 6.11). The integrated intensities of the two sites in CM5 and CM10 are approximately 70:30, consistent with the ratio found for the narrow resonances, CsNaMoO$_4$(l) and Cs$_3$Na(MoO$_4$)$_2$, observed in the $^{23}$Na MAS NMR, (Table 6.3). CM3 does not show evidence of Cs$_3$Na(MoO$_4$)$_2$; this is attributed to the poor signal-to-noise ratio of the spectrum.
Figure 6.11: Comparison of HT $^{133}$Cs MAS NMR of phase separated model waste samples (CMx) and pure crystal phase of CsNaMoO$_4$·2H$_2$O studied in chapter 5.
$^{23}$Na NMR implies that the total crystallinity is constant between the room and high-temperature experiments. Provided the crystallinity is constant, the cesium ions in the unidentified phases noted in the 14.1 T $^{133}$Cs spectra must be incorporated into the one or two liquid resonances identified in the high-temperature spectra. The narrow resonance in the $^{133}$Cs MAS NMR above 500°C indicate that the Cs$^+$ ions are likely mobile, hopping between sites in the crystalline phases. $^{23}$Na NMR at these temperatures indicates that the bulk glass component of these materials remains solid, therefore the Cs$^+$ ions are not expected to interact with this portion of the phase. As the ions move between the various crystalline sites the observed NMR resonance will be that of their average interaction. The only sodium-bearing crystalline phases across the CMx series are Cs$_3$Na(MoO$_4$)$_2$ and Na$_2$MoO$_4$, therefore, the average $^{23}$Na NMR chemical shift is constant for the melt, since there is minimal change in the average Na$^+$ environment.

For the Cs$^+$ ions the number of cesium-bearing phases increases across the glass series, consistent with the change in the chemical shift of the melt resonances. A strong correlation, $R^2 = 0.97$, was found between the average $^{133}$Cs chemical shift, $\delta_{\text{avg}}$, for the high-temperature resonances and the $\delta_{\text{avg}}$ for the room temperature crystalline phases identified in the 14.1 T data (Figure 6.12). $\delta_{\text{avg}}$ for the room temperature $^{133}$Cs data was calculated by weighting the $\delta_{\text{iso}}$ of the various resonance by their integrated intensities. The integrated intensity of the CsNaMoO$_4$·2H$_2$O resonance was converted into the weighted average of the resonances for the Cs$_3$Na(MoO$_4$)$_2$ phase ($\delta_{\text{avg}} = 30.3$ ppm), since this is the phase
that will be present above 100°C. This correlation appears to confirm that the observed $^{133}$Cs resonance for the high-temperature phases is influenced primarily by the composition and structure of the polycrystalline phase from which it was formed.

![Correlation of room temperature $^{133}$Cs $\delta_{\text{avg}}$ and high-temperature $\delta_{\text{avg}}$ (temperatures are reported in table 6.3). Red points indicate the $^{133}$Cs $\delta_{\text{avg}}$ for the CMx series, while the green point indicates the $\delta_{\text{avg}}$ for CsNaMoO$_4$·2H$_2$O upon conversion to Cs$_3$Na(MoO$_4$)$_2$ after dehydration. The applied linear trend-line has a coefficient of determination, ($R^2$), of 0.97.](image)

### 6.5.3 Implications

From the $^{23}$Na and $^{133}$Cs MAS NMR data, it can be seen that all of the crystalline phases in these samples appear to transform into only one or two liquid phases at
high temperatures. This mechanism is likely analogous to the process by which these crystalline phases precipitate during the formation of these materials. The formation of nuclear waste forms and their model analogues occurs at very high temperatures (1100 - 1300°C), followed by cooling at ≤1°C/minute, (see chapter [1]). The lack of change between the integrated intensities of the crystalline and glassy resonances in the $^{23}$Na MAS NMR suggest that the glass is still solid in all the experiments where liquid phases were observed. These results are consistent with the glass transition temperatures for these materials, which are expected to be between 600-700°C for alkali borosilicate glasses with $K \approx 4$ and $R \approx 0.6 - 1.1$, (Table 6.2).[109] Both Cs$_3$Na(MoO$_4$)$_2$ and Na$_2$MoO$_4$ crystalline phases have melting points around 700°C, (see section 5.4), but, as was demonstrated in the CsNaMoO$_4$·2H$_2$O example in chapter 5, the melting point of the two phases intermixed is closer to 575°C.[84] Therefore, upon cooling the liquid wasteform mixture, it is expected that the glass will solidify prior to the crystallization of these crystalline molybdate phases. As the glass solidifies the molybdate phases remain liquid as inclusions within the bulk glass matrix. These liquid inclusions will contain a mixture of cesium, sodium and molybdenum, which precipitate as various crystalline phases upon cooling below their crystallization temperatures. A schematic describing this process is provided in figure 6.13.
The results in chapter 5 show that the CsNaMoO$_4$($l$) phase grows above 500°C with increasing temperature upon the heating of CsNaMoO$_4$·2H$_2$O, while Cs$_3$Na(MoO$_4$)$_2$
and \( \text{Na}_2\text{MoO}_4 \) are prominent in the spectra at lower temperatures. Upon cooling a nuclear wasteform (or model system) the reverse process is expected, with the \( \text{CsNaMoO}_4(l) \) phase being the dominant phase in the liquid inclusions. The \( \text{CsNaMoO}_4(l) \) phase is expected to disproportionate into the two primary crystalline phases observed in room temperature \( ^{23}\text{Na} \) and \( ^{133}\text{Cs} \) spectra: \( \text{Cs}_3\text{Na}({\text{MoO}}_4)_2 \) and \( \text{Na}_2\text{MoO}_4 \). \( \text{Na}_2\text{MoO}_4 \) and \( \text{Cs}_3\text{Na}({\text{MoO}}_4)_2 \) have similar melting points, 689\(^\circ\)C \cite{84} and \( \approx 750\,\text{°C} \) (see chapter 5), respectively. This is inconsistent with the HT \( ^{23}\text{Na} \) and \( ^{133}\text{Cs} \) MAS NMR of \( \text{CsNaMoO}_4\cdot2\text{H}_2\text{O} \) which indicates that \( \text{Cs}_3\text{Na}({\text{MoO}}_4)_2 \) melts at temperatures as low as 550\(^\circ\)C when part of a polycrystalline mixture. This suggests that upon cooling of the \( \text{CsNaMoO}_4(l) \) phase, \( \text{Na}_2\text{MoO}_4(s) \) will precipitate from the liquid first. NMR also suggests that the \( \text{CsNaMoO}_4(l) \) and the highly mobile \( \text{Cs}_3\text{Na}({\text{MoO}}_4)_2 \) phases exist simultaneously, with the low-temperature \( \text{Cs}_3\text{Na}({\text{MoO}}_4)_2(s) \) phase forming at much lower temperatures, as low as 300\(^\circ\)C in the CM10 glass. In the case of higher molybdenum content glasses this process is complicated by the formation of various other molybdate phases. Since the CMX series indicates there is only one or two common liquid phases found at high temperatures which produce the multitude of crystalline phases, the crystallites are expected to be formed as mixed polycrystalline inclusions within the bulk glass. The resulting polycrystalline inclusions are expected to be formed primarily of \( \text{Cs}_3\text{Na}({\text{MoO}}_4)_2 \) and \( \text{Na}_2\text{MoO}_4 \). The presence of these two primary phases in close proximity allows for the formation of \( \text{CsNaMoO}_4\cdot2\text{H}_2\text{O} \) upon exposure to water in ambient conditions.
6.5.4 Conclusions

Over a diverse data set of complicated phase separated glasses, a common response to high temperatures has been observed via $^{133}\text{Cs}$ and $^{23}\text{Na}$ MAS NMR. The phase separation in these model nuclear waste glasses appears to be the product of one or two liquid phases. During the initial formation of these materials it is expected that these high-temperature phases remain as liquid inclusions below the glass transition temperature of the bulk material.
Chapter 7

Impact and Future Outlook

The projects covered in this thesis demonstrate the capabilities, power and versatility of NMR and particularly some novel applications of high-temperature MAS. From our studies it is clear that high-temperature MAS NMR can be effective at measuring phase changes, dynamics and chemistry in solid materials. Furthermore, chapter 6 shows some of the first applications of HT-NMR to mixed phase materials. This work also provides the unique observation of high-temperature fluids enclosed within a bulk vitreous material.

7.1 Impacts for the Nuclear Industry

This work has direct implications for the processing and storage of nuclear waste materials. It has been previously indicated that as the glass-waste melt is cooled
the glass can phase-separate forming distinct molybdenum rich domains.\cite{6, 7, 25}

These domains form hygroscopic polycrystalline molybdate phases upon reaching room temperature.\cite{25} From our work we have shown that these crystalline molybdate phase appear to have a lower melting point than the bulk glass. It was observed that in our model systems the bulk glass can remain solid up to at least 650°C, while the molybdates become liquid at temperatures as low as 500°C. This observation implies that as the nuclear waste material is cooled during vitrification the bulk glass solidifies while the molybdate domains remain liquid. These liquid inclusions may be relatively long-lived, as the nuclear waste material can have centerline temperatures above 400°C for the initial period after their creation.

The presence of liquid inclusions in a bulk glass matrix has been studied in several other types of materials, including model volcanic glasses.\cite{110, 111, 112} It was found that the introduction of gas (CO$_2$ or Xe) or liquid (H$_2$O) inclusions into a sodium-potassium aluminosilicate glass resulted in a reduction in glass strength of almost three orders of magnitude.\cite{112} Heating these vesicular glasses caused the pressure within these inclusions to increase, in some cases leading to \textit{decrepitation}, i.e., the collapse of the inclusion. The “popping” of these inclusions could be sufficiently violent in some cases to disintegrate the sample into a fine powder.

For industrial purposes it is obvious that liquid inclusions could be fatal to the durability of these radioactive waste forms. The centerline temperatures for nuclear waste storage materials are estimated to be $\approx$400°C under an active cooling
system. The possible failure of these cooling systems during the initial storage years could cause an increase in these temperatures, which could give rise to the formation of CsNaMoO$_4$(l) (which was observed at temperatures as low as 500°C). In a “worse-case” scenario, where the temperature of these storage materials was allowed to increase, the expansion of these liquid molybdate inclusions could result in cracking of the bulk glass, exposing soluble cesium to the surface of the glass. Any increase in the surface area of these materials will increase the possibility of contamination in the case of water seepage into the containment facility.

The high temperatures of radioactive waste materials also means that for at least the “near-future” (< 10,000 yr) the materials will be >200°C. At these high temperatures any contact with water, either through ground water seepage or through ambient humidity, will result in vaporization. At these temperatures the formation of CsNaMoO$_4$·2H$_2$O will not be possible. Once the material reaches temperatures below 100°C the possibility for the formation of the crystalline phase CsNaMoO$_4$·2H$_2$O increases.

### 7.2 Further Work on Crystalline Molybdates

Chapter 4 presents the successful characterization of a selection of crystalline molybdate phases. This study could be expanded to incorporate more molybdate phases, including Cs$_2$Mo$_4$O$_{13}$, Cs$_2$Mo$_3$O$_{10}$, Cs$_2$Mo$_5$O$_{16}$ and Cs$_2$Mo$_2$O$_7$. These
phases would be particularly useful to expand the trends in $^{133}$Cs MAS NMR parameters studied, due to the limited size of the analyzed data set. Furthermore, exploring the CSA parameters for $^{133}$Cs NMR for these phases could be useful in characterizing the local structure of the Cs$^+$ ions. From some preliminary work it was found that the CSA parameters were challenging to extract in the studied materials due to the additive effects of CSA, quadrupolar coupling and dipolar couplings present in non- and slow-spinning spectra. For the assessment of CSA parameters $^{133}$Cs MAS NMR spectra would need to be collected at slow spinning rates ($\approx$3-5 kHz) and multiple field. These spectra would than need to be fitted systematically using an appropriate fitting software, e.g., STARS or DMFit.\cite{113-116} In addition to $C_Q$, $\eta$, $\Omega$, $\kappa$ and $\delta_{iso}$, the Euler angles would also need to be assessed.\cite{56}

Quantum mechanical calculations would be an effective and possibly necessary addition to the study of the crystalline molybdate phases. These calculations would need to incorporate an appropriate relativistic method, such as ZORA (Zeroth-Order Regular Approximation).\cite{117} Due to the crystalline nature of these phases, it would be ideal to employ periodic boundary conditions and plane-wave basis sets for the calculations for these materials. One of the leading codes for calculations of this type is CASTEP, which has successfully been applied to a wide variety of NMR studies of crystalline materials.\cite{118-120} From calculations, the orientation and structural dependencies of the chemical shielding and EFG tensors could be determined, which may provide further insight into the observed spectra.
7.3 Further High-Temperature NMR Work on Crystalline Molybdates

The high-temperature MAS NMR data set for this series of crystalline molybdates is relatively complete. $^{95}$Mo MAS NMR spectra was not collected for Cs$_2$MoO$_4$ due to the clarity of the $^{133}$Cs data, but its addition to the series could be useful in understanding the high-temperature behaviour of molybdate units. $^{23}$Na MAS NMR was found to be particularly effective for studying high-temperature phase transitions, therefore additional sodium-bearing crystalline molybdates could be a fertile area of study. Na$_2$Mo$_2$O$_7$ and Na$_2$Mo$_4$O$_{13}$ are two crystalline phases with well characterized high-temperature behaviours, which could be studied by $^{23}$Na NMR. High-temperature $^{133}$Cs MAS NMR were also found to be effective at studying dynamics and phase transitions, therefore the series of phases could also be expanded to include more cesium-bearing molybdates, (see examples above). Sodium tungstates have also been shown to have similar NMR parameters as molybdates due to their isoelectronic structure. The behaviour of Na$_2$WO$_4$ under high temperatures is well documented and would likely provide a satisfactory study by $^{23}$Na MAS NMR.\cite{121}

Although rubidium molybdates are not relevant to nuclear waste phase separation, they are isoelectronic with sodium and cesium analogues and could prove to be a profitable area of study. $^{87}$Rb is a particularly sensitive quadrupole nucleus with a relatively high natural abundance, resonance frequency and moderate quadrupole
moment (Table 7.1). Additionally, $^{87}\text{Rb}$ tends to have relatively short $T_1$'s, typically allowing for acquisition of relatively high signal-to-noise spectra with relatively narrow MAS central-transition centerbands. These properties could lead to similar spectra as the $^{23}\text{Na}$ MAS NMR experiments described in chapters 4 and 5.

**Table 7.1: Properties of NMR Active Isotopes of Rubidium.**

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Spin</th>
<th>Resonance Frequency at 9.4T (MHz)</th>
<th>Quadrupole Moment (mb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{85}\text{Rb}$</td>
<td>5/2</td>
<td>38.8</td>
<td>276</td>
</tr>
<tr>
<td>$^{87}\text{Rb}$</td>
<td>3/2</td>
<td>131.4</td>
<td>133.5</td>
</tr>
</tbody>
</table>

### 7.4 Further Work in Model Nuclear Waste Systems Using High-Temperature NMR

The series of materials studied in chapter $\text{6}$ provide a preliminary range of simplified compositions. By expanding the composition series to include materials with 5% MoO$_3$ : 10% Cs$_2$O and 10% MoO$_3$ : 5% Cs$_2$O, the effects of Cs$_2$O and MoO$_3$ on the high-temperature melts could be isolated. Additionally, investment in $^{95}\text{Mo}$-enriched MoO$_3$ could be used to produce materials which would have sufficient sensitivity to be studied by $^{95}\text{Mo}$ MAS NMR.

It may also be worth exploring the changes in glass structure for these materials using HT $^{11}\text{B}$ and $^{29}\text{Si}$ MAS NMR. The lack of interaction expected between the
crystalline and vitreous phases would likely produce relatively uneventful results. $^{29}\text{Si}$ MAS NMR will be particularly challenging since the natural abundance is low (4.7\%) and $^{29}\text{Si}$ tends to have long $T_1$’s.

Ruthenium is an expected daughter product of $^{235}\text{U}$ and can be paramagnetic, which interferes with NMR measurements through broadening and shifting of the spectra. The paramagnetic interaction is typically quite sensitive to temperature, allowing for structural data to be interpreted from its measurement. Studying a series of model nuclear waste glasses with small amounts of RuO$_2$ (1-5 wt. \%) by $^{11}\text{B}$, $^{29}\text{Si}$, $^{23}\text{Na}$ and $^{133}\text{Cs}$ MAS NMR should result in broadening of either the glass or crystalline peaks.\[25] High-temperature MAS NMR should be able to measure the change in relaxation times (both $T_1$ and $T_2$) with temperature for both the glass and crystalline phases. From the comparison of these data it should be possible to make some conclusions on the distribution of Ru$^{4+}$ ions amongst the different phases. This type of study could be repeated or adapted for any of a number of common paramagnetic ions in HLW.

7.5 NMR Applications in HT chemistry

High-temperature NMR shows promise in a variety of other applications, particularly in the \textit{in situ} observation of high-temperature solid-state chemistry. As noted earlier, Cs$_3$Na(MoO$_4$)$_2$ is particularly challenging to synthesize in high purity. A possible project could be the careful observation of the temperature dependence
of a mixture of Na$_2$MoO$_4$ and Cs$_2$MoO$_4$ by $^{133}$Cs or $^{23}$Na MAS NMR. This could provide insight into the reaction mechanism that produces Cs$_3$Na(MoO$_4$)$_2$ and hopefully indicate the limiting factor of the reaction.

HT MAS NMR would also be a suitable technique for studying cation mobility. Variable temperature $^7$Li NMR has already been successfully applied to conductivity in a variety of materials.\textsuperscript{122–127} $^7$Li NMR is particularly useful for HT studies due to its high sensitivity and prevalence in conductive materials. Unfortunately, it is also a highly competitive field with an extensive NMR history. For example, lithium niobates have been studied, by high-temperature $^7$Li NMR, continuously since the early 1970s.\textsuperscript{128–131}

Therefore, it may be most profitable to study ion conductivity in less traditional materials. Li$_2$S$_x$-P$_2$S$_5$$_{1−x}$ based vitreous and ceramic materials have shown promise as solid electrolytes.\textsuperscript{132, 133} These materials could be investigated by a combination of $^7$Li and $^{31}$P HT MAS NMR. $^7$Li NMR can be spectroscopically challenging due to the strong broadening effects from the homonuclear dipolar couplings. $^6$Li NMR does not suffer from this type of broadening due to the lower resonance frequency and lower natural abundance.\textsuperscript{65} By enriching the material with $^6$Li the sensitivity of the $^6$Li NMR would be increased, while the homonuclear dipolar coupling for $^7$Li NMR would be reduced. It would therefore be ideal to study a series of $^6$Li enriched Li$_2$S$_x$-P$_2$S$_5$$_{1−x}$ by a combination of $^6$/7Li and
$^{31}\text{P}$ MAS NMR at high-temperatures. Room temperature studies and conductivity measurements were performed by Eckert et al. in 1990 on a similar series of these materials.\cite{134} Recently, it has been found that raising these materials above 210°C for extended periods of time resulted in the precipitation of temperature dependent nanocrystalline phases within the bulk glass matrix, creating glass-ceramics with improved conductivity.\cite{135} Furthermore, the addition of P$_2$O$_5$ into these materials was found to increase conductivity. These materials have encouraged several other studies in similar materials, but there has been no attempt to characterize this precipitation \textit{in situ} using HT MAS NMR.\cite{136, 137}
Bibliography


