Applications of Si-29 Magic-Angle Flipping NMR Experiments to Silicate Glasses

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Abstract

Various alkali and alkaline earth modified silicate glasses were studied using Si-29 Magic-Angle Flipping Nuclear Magnetic Resonance (MAF-NMR) spectroscopy. The chemical shift anisotropy (CSA) trends were extracted for glasses with a variety of $Q^{(4)}$, $Q^{(3)}$, and $Q^{(2)}$ sites. We observed that the CSA increases roughly linearly with respect to cation potential (cation charge divided by cationic radius). In a mixed glass consisting of K_2O and MgO modifiers, significant ordering was found for the cations near the non-bridging oxygen atoms on $Q^{(3)}$ sites. In particular we see one $Q^{(3)}$ site with a CSA similar to a pure K_2O modified glass and a second site with a CSA that is the average of K_2O and MgO modified glass CSA values. This proves that one of the sites has only K^+ modifiers while the other is a mixture of K^+ and Mg^{2+} modifying cations. This shows a remarkable degree of ordering in a disordered system such as this. Recent studies of Cs_2O modified glasses suggest that even with a single modifying cation there may be multiple kinds of $Q^{(3)}$ coordination environments. Again, having distinct coordination environments is surprising and shows that these glasses often posses greater ordering than expected for a purely random model.

Introduction

In Si-29 MAS NMR individual peaks are observed for different Si-29 environments characterized by the number of bridging oxygen atoms linking SiO_4 tetrahedra. We assign each peak as a $Q^{(n)}$ with n counting the number of bridging oxygen atoms and ranging from 0 to 4, depending on the amount of modifier cations present. The microscopic distribution of $Q^{(n)}$ sites is correlated with macroscopic properties such as hardness, glass transition temperature, or bulk density. As modifier cations such as Na^+, K^+, or Mg^{2+} are added to a SiO_2 glass, the pure $Q^{(4)}$ network is depolymerized producing more and more $Q^{(3)}$ and ultimately $Q^{(2)}$ sites, reducing the melting point from over 1600C to under 1000C in some cases. The depolymerization may be binary (all $Q^{(4)}$ makes $Q^{(3)}$ before any $Q^{(2)}$ is made, etc.) or random (many different $Q^{(n)}$ are present in a given composition) depending on the cation potential of the modifier. At OSU, we have been developing improved methodologies to extract the $Q^{(n)}$ speciation data from silicate glasses using MAF and MAT experiments combined with echo train detection. We believe the improved accuracy of these distributions will lead to a better understanding of the underlying glass structures in these materials.

Experimental

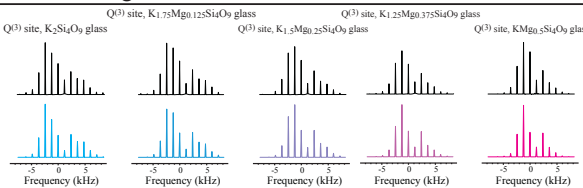**2D MAF-CPMG**   **MAT-PIETA**
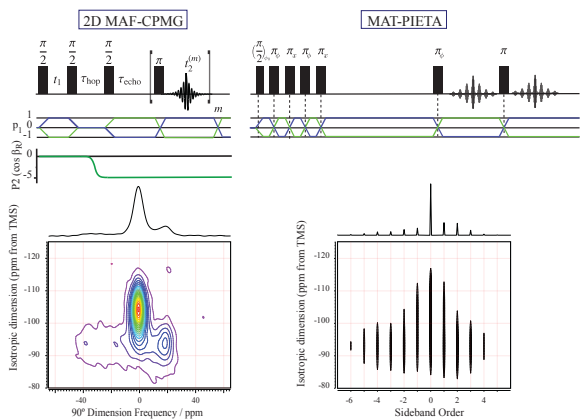
In the standard Magic-Angle Spinning (MAS) experiments the anisotropic information is averaged by rapid sample rotation at an angle of 54.74° with respect to the static magnetic field. In amorphous sample such as the tetra silicate glasses the individual $Q^{(n)}$ species cannot be easily separated in a MAS experiment. To accomplish the appropriate Q species resolution, our samples were studied with the Magic Angle Flipping (MAF) experiment utilizing a home-built probe in the Grandinetti lab at the Ohio State University with CPMG echo train acquisition. In this experiment, the isotropic MAS spectrum is correlated in a second dimension with the anisotropic spectrum taken while the rotor spin at an angle of 90° with respect to the external field. The pulse sequence for this is shown above to the left along with an example of an MAF spectrum of a potassium tetra silicate glass. The primary advantage of MAF is that we can clearly distinguish the narrow $Q^{(4)}$ site from the broad $Q^{(3)}$ site in the anisotropic dimension even though they overlap significantly in the isotropic MAS dimension.

A second experiment called Magic Angle Turning Phase Incremented Echo Train Acquisition (MAT-PIETA) was used to study the same compounds as a comparison to the MAF experiment. The advantage of MAT-PIETA is higher sensitivity along with using a conventional MAS probe instead of a flipping probe. We hope to show that identical information can be extracted from both experiments and thus allow MAT-PIETA to largely replace MAF in the general world. The pulse sequence for MAT-PIETA is shown above to the right along with the 2D spectrum for the same potassium tetra silicate glass. It is clear that the overall line position in the anisotropic dimension fall on top of the anisotropic lineshape from the MAF.

Results and Discussion

Potassium/ Magnesium Silicate Glasses

$Q^{(3)}$ site, $K_2Si_4O_9$ glass $Q^{(3)}$ site, $K_{1.75}Mg_{0.125}Si_4O_9$ glass $Q^{(3)}$ site, $K_{1.5}Mg_{0.25}Si_4O_9$ glass $Q^{(3)}$ site, $K_{1.25}Mg_{0.375}Si_4O_9$ glass $Q^{(3)}$ site, $KMg_{0.5}Si_4O_9$ glass
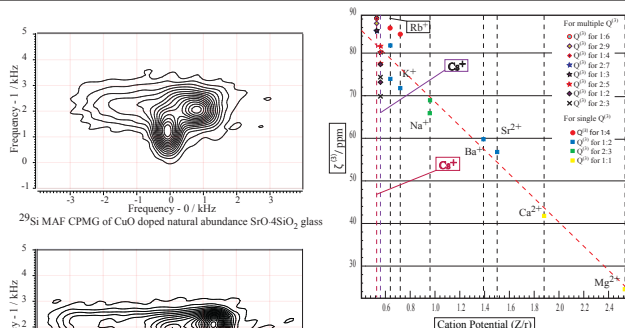
Results from the MAT-PIETA experiments contrasted with simulations based on the double $Q^{(3)}$ site model.

In a previous MAF study, Keeler and coworkers demonstrated that in a mixed potassium/magnesium tetra silicate glass there exists only two types of $Q^{(3)}$ sites. One site arises from a $Q^{(3)}$ site coordinated by potassium only while the other $Q^{(3)}$ site comes from a 2:1 mixed K/Mg coordination environment. Here we compare the MAT slices with simulations assuming site population from the MAF study. The agreement between experiments and fits shows that MAT-PIETA can give comparable results to MAF.
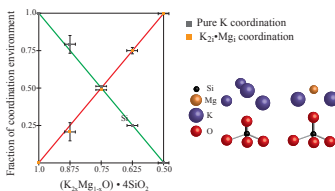
ABOVE: $Q^{(3)}$ binary site model for K/Mg mixed tetrasilicate glasses. The two site model suggests that a given non-bridging oxygen site is coordinated by a limited number of distinct possibilities.
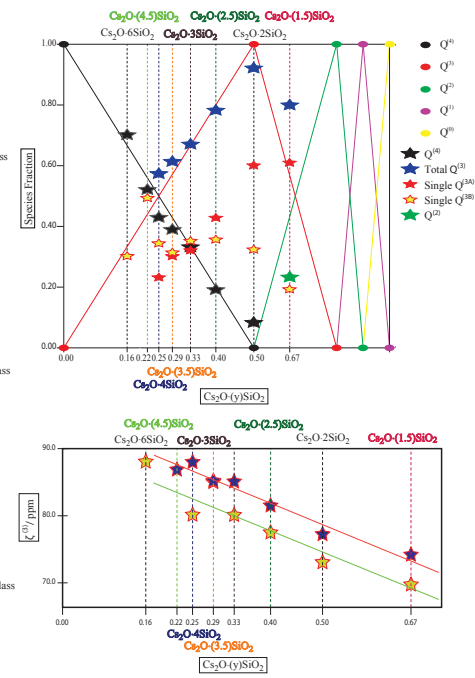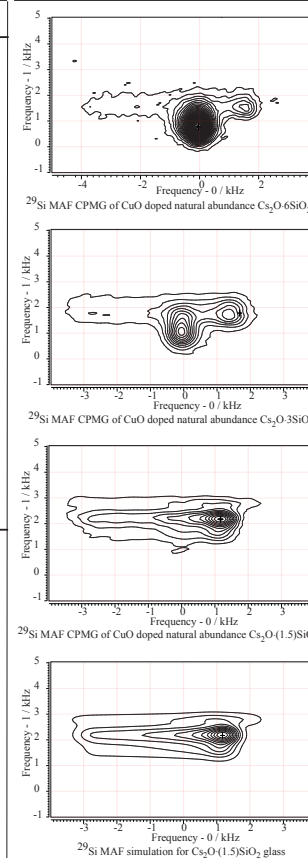
■ Pure K coordination
■ $K_2 \cdot Mg_1$ coordination

● Si   ● Mg   ● K   ● O

Alkali and Alkaline Silicate Glasses

^{29}Si MAF CPMG of CuO doped natural abundance $SrO \cdot 4SiO_2$ glass

^{29}Si MAF CPMG of CuO doped natural abundance $Rb_2O \cdot 4SiO_2$ glass

^{29}Si MAF CPMG of CuO doped natural abundance $Na_2O \cdot 2SiO_2$ glass

MAF studies have been conducted on a range of alkali and alkaline earth modified tetra silicate glasses. Simulation of the spectra have allowed us to extract a parameter zeta which is a measure of the overall chemical shift anisotropy of a $Q^{(3)}$ site. In particular, Keeler and coworkers have shown that zeta is strongly dependent on the Si-O non-bridging bond length. Our observation is that zeta scale roughly proportional to the cation potential (cation charge divided by the Pauling cation radius). This result agrees with the fundamental understanding that the most electropositive cations form purely ionic bonds with coordinating oxygen atoms leading to shorten Si-O non-bridging bond lengths. In addition, in some of the glasses evidence was observed that there may be multiple $Q^{(3)}$ sites corresponding to different coordination numbers for the large cationic partners. If this hypothesis holds true then it implies that there is significant orderings in the amorphous materials.

Cesium Silicate Glasses

^{29}Si MAF CPMG of CuO doped natural abundance $Cs_2O \cdot 6SiO_2$ glass

^{29}Si MAF CPMG of CuO doped natural abundance $Cs_2O \cdot 3SiO_2$ glass

^{29}Si MAF CPMG of CuO doped natural abundance $Cs_2O \cdot (1.5)SiO_2$ glass

^{29}Si MAF simulation for $Cs_2O \cdot (1.5)SiO_2$ glass

The MAF-CPMG experiments of Cesium glasses show that there are two types of $Q^{(3)}$ sites in these glasses. Our best explanation is that the separate sites arise from the difference in cesium coordination due to its large cationic radius. It is interesting to note that the cesium glass (much like previously studied sodium and potassium glasses) seems to show a nearly binary Q speciation. Meaning that very little $Q^{(2)}$ sites are seen until the composition has enough cesium to convert all $Q^{(4)}$ sites into $Q^{(3)}$. The two types of $Q^{(3)}$ sites do not appear to follow a similar binary relation. These observations place significant constraints on possible microscopic structural models that might be possible for these glasses.

Conclusion

We obatained the Si-29 MAF-CPMG from eight cesium silicate glass samples during the summer and found the nature of Q species especially the interesting $Q^{(3)}$ co-ordinations. We suspect that there may be more than one $Q^{(2)}$ coordination in silicate glasses with very high cesium composition. Now we are continuing this cesium study with Sanders from The Ohio State University by doing sample simulations for him. We anticipate doing MAF experiments with samples which have lower cesium content than that in $Cs_2O \cdot 6SiO_2$, and also with sample which have higher cesium content than that in $Cs_2O \cdot (1.5)SiO_2$ to complete the cesium Q speciation charts and observe the number of coordination in Q species as well as the glass structure. However, silicate glass with high silica content have high melting point. Also silicate glasses with high cesium compositions are very hygroscopic; thus, we need to be careful with quenching and storing these glasses with high cesium content. Also, we plan to do MAT experiments with these cesium glasses and compare those results to the results from the MAF-CPMG experiments of the same cesium glasses. Therefore, we can compare the two methods and assure whether MAF-CPMG can be replaced by the MAT-PIETA.

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