NMR Studies of Pyrophosphate and Tetrasilicate Glasses

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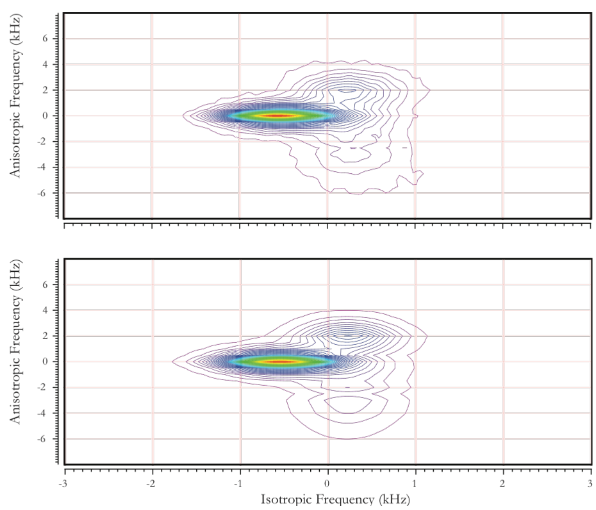
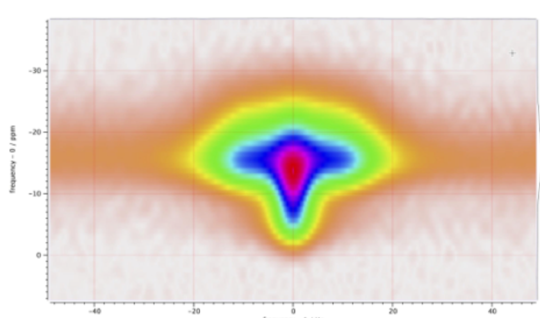
My research during the summer of 2017 was conducted with three students (Sara Garner, Tomas Flores, and Shay Steele) for 10 weeks from early-May to mid-July. As in prior years, my focus was to synthesis new phosphate based glasses and crystalline compounds to study using PASS (Phase Adjusted Spinning Sidebands) and TE-PIETA (Total-Echo Phase Incremented Echo Train Acquisition). The former is used to measure the chemical shift anisotropy (CSA) and the later measure the homonucleare J-coupling constants in these phosphate samples. The most significant change in my current research was the replacement of the original PIETA experiment with the new TE-PIETA version. We tested some of the older samples with this new version of the experiment to quantify the improvement in overall spectral quality (which seems to be significant). We also have continued to refine my PASS simulation software to include a full extended Czjzek distribution for the CSA. This software was used to extract the CSA parameters from both current phosphate glass samples as well as some older silicate based glass data taken at the Ohio State University in a prior summer.

An important outcome of our work this summer was to confirm that in a mixed potassium magnesium tetrasilicate glass ($K_{2-2x}Mg_xSi_4O_9$ formula with x from 0 to 0.5) has been shown with ^{17}O experiments that there are two distinct non-bridging oxygen envrionments corresponding to the $x = 0$ and $x = 0.5$ compositions and mixtures of these are simply mixtures of these two kinds of environments (rather than an average of them). This is significant because it implies there is a much greater degree of order in this glass than one might expect. By using the PASS experiment (along with a Magic-Angle Flipping experiment a few years ago), we have confirmed that this model is consistent with the observed ^{29}Si data where the CSA pattern observed for intermediate compositions is a linear combination of the same end group members as in the ^{17}O experiments.



Anisotropic PASS spectrum of $K_{1.25}Mg_{0.375}Si_4O_9$ showing original data (top) and simulation (bottom). This simulation uses a three site model since the two site model gave physically unrealistic CSA parameters.

The new glasses measured this summer were a variety of compositions but we focused on $Na_4P_2O_7$ and $Pb_2P_2O_7$ compositions as well as a linear combination of these end group members. The fundamental question was whether a phosphate glass might sow the same sort of trends we saw in the tetrasilicate glass. Our initial results seem to demonstrate there seem to be multiple distinct J-coupling distributions present for the intermediate composition glasses. This seems not to be as apparent in the CSA distrubtions observed for these same mixed glasses because the endgroup distributions seem to be far more similar than in the tetrasilicate glasses. The mixed silicate results are now completed to the point they can be written up for publication while the phosphates are probably not sufficiently studied.



2D NMR PE-PIETA experimental data for a $NaPb_{1.5}P_2O_7$ glass.