Measurement of J-coupling in Mixed Lead and Sodium Pyrophosphate Glasses with PASS and TE-PIETA.

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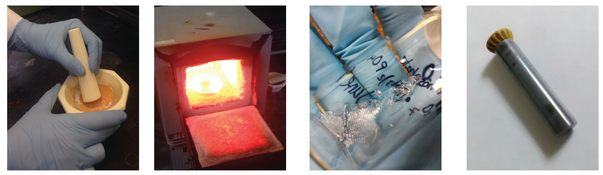
Introduction

Phosphate glasses have a distribution of bond angles which make probing the structural parameters of amorphous materials difficult via traditional NMR experiments. The Total-Echo Phase Incremented Echo Train Acquisition (TE-PIETA) Nuclear Magnetic Resonance (NMR) experiments provide a method to measure the ^{31}P homonuclear J-coupling which is then used to determine medium range structural information. In particular, this J-coupling distribution is strongly correlated with the P–O–P bond-angle distribution. Throughout the summer, we used TE-PIETA to measure the correlation of J-couplings with isotropic chemical shift of varying compositions of sodium, lead and phosphate glasses. The hypothesis proposed was that the mixed metal phosphate glasses would have two environments with different J-coupling patterns, specifically regions rich in Pb^{2+} and other regions with both Na^{+} and Pb^{2+} ions. The pyrophosphate samples were synthesized by mixing solid compounds of varying Pb^{2+} and Na^{+} ions. We have also used Phase Acquisition Spinning Sideband (PASS) experiments to find additional chemical shift anisotropy information with isotropic chemical shift.

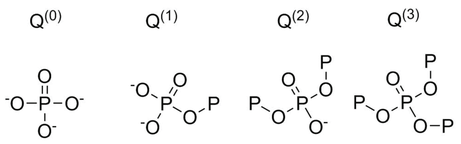
Experimental

The glass samples were created by mixing varying amounts of pyrophosphate with select transition metals to form specific chemical ratios which would promote desired Qn Series goal.



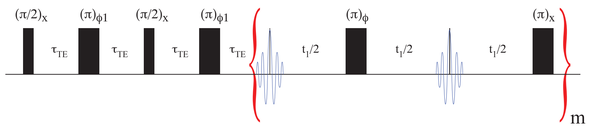
Q Series

Q^n notation refers to the number of bridging oxygen atoms that separate the phosphate tetrahedral. $Q^{(0)}$ would signify a phosphate site while $Q^{(1)}$ represents the presence of one bridging oxygen or a pyrophosphate.

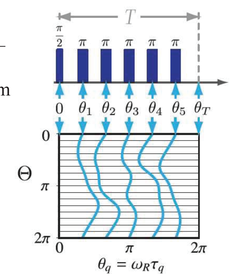


TE-PIETA and PASS Pulse Sequence

The TE-PIETA is a pulse sequence with two phase dimensions, one to refocus both J-coupling and chemical shift (ϕ_1) and the other to create an echo train with J-coupling evolution (ϕ) in the t_1 dimension. This creates a 4-dimensional data set which reduces to a 2-dimensional J-resolved experiment with appropriate phase processing.

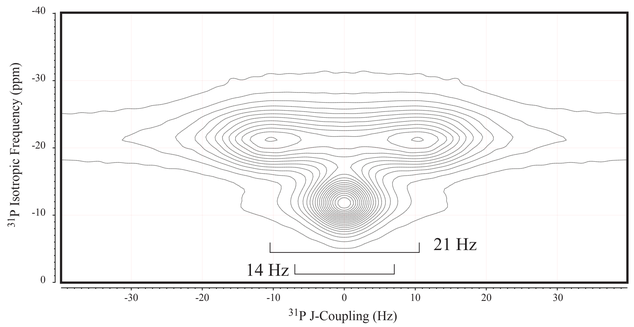


The PASS experiment is the correlation of chemical shift anisotropy with isotropic chemical shift. 5 π pulses occur with slow magic angle spinning to project interactions in all three dimensions.

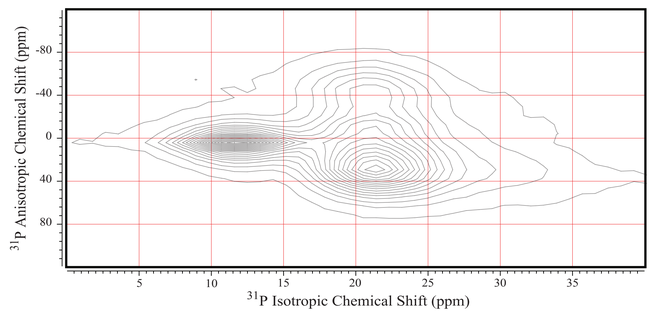


TE-PIETA and PASS Spectra of Na/Pb Mixed Pyrophosphate Glasses

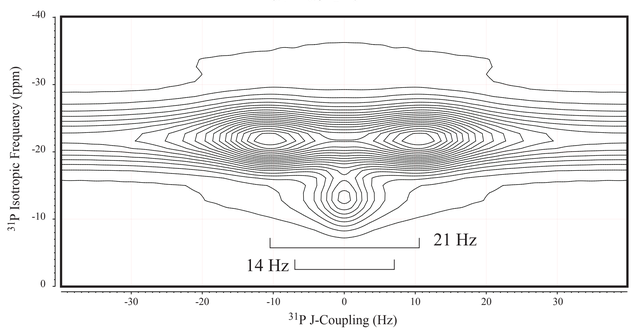
$Pb_2P_2O_5$ TE-PIETA



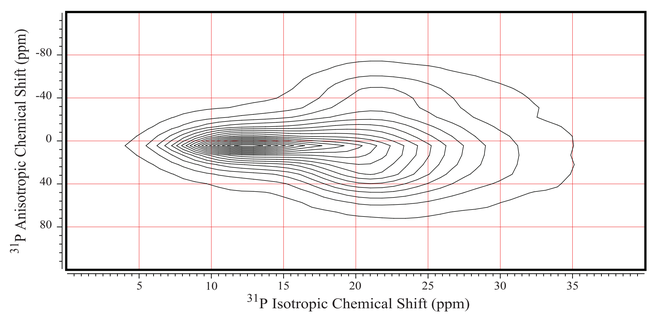
$Pb_2P_2O_5$ PASS



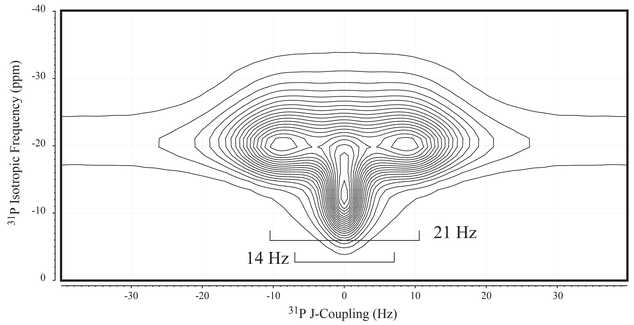
$Na_{0.4}Pb_{1.8}P_2O_5$ TE-PIETA



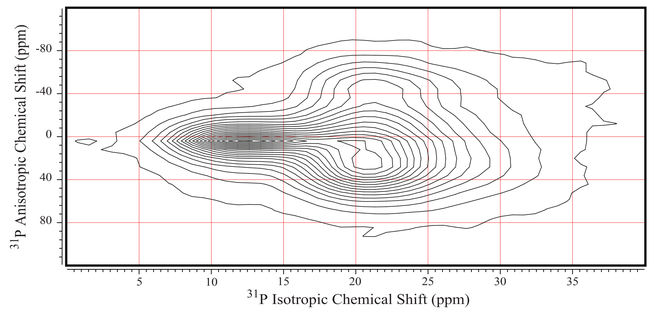
$Na_{0.4}Pb_{1.8}P_2O_5$ PASS



$Na_{0.8}Pb_{1.6}P_2O_5$ TE-PIETA



$Na_{0.8}Pb_{1.6}P_2O_5$ PASS



Results

We can observe that the TE-PIETA data includes two types of J-coupling patterns. The Pb rich region has a J-coupling around 21 Hz (see pure Pb spectrum), while a second pattern emerges around 14 Hz as Na is added. This mixed cation region corresponds to a lower phosphate-oxygen bond angle within the glass (from prior J-coupling simulations). By looking at the data is it hard to indicate whether the samples is a glass with two separate phase or a glass homogenized. The PASS data indicates that the change of sodium concentration does not greatly affect the CSA of our samples. Within our samples there also appears to be a triphosphate region near –30 ppm in the isotropic dimension indicating $Q^{(2)}$ sites within the glass.

Conclusion

The sodium and lead pyrophosphate glass series was our main focus over the summer. The initial hypothesis proposed was that the mixed metal phosphate glasses would have two regions of J-coupling patterns. Rich regions of Pb^{2+} and another region with both Na^{+} and Pb^{2+} patterns. The pyrophosphate samples were synthesized by mixing solid compounds of varying Pb^{2+} and Na^{+} ions. The data indicates that there are two J-coupling but very little CSA change within the samples. Unfortunately the reproducibility of this data was difficult to achieve due to challenges in the fast quench rate required. We have begun construction of a roller bar quencher that will allow us to make samples with higher reproducibility for additional solid state NMR experiments.