NMR Studies of Crystalline Pyrophosphate Salts

Jay Baltisberger

My research during the summer of 2015 was conducted with one student (Kodey Blankenship) for 10 weeks from early-May to mid-July. The primary objective was to develop a protocol for synthesis and characterization of pyrophosphate salts ($Sn_2P_2O_7$, $Ba_2P_2O_7$, $Zn_2P_2O_7$, $Pb_2P_2O_7$, $Na_4P_2O_7$, and $Ca_2P_2O_7$). Two synthetic approaches were used, one being an aqueous low temperature method and the other a solid-state high temperature technique (figure 1 demonstrates that the high temperature method produces a crystalline $Pb_2P_2O_7$ sample that is highly homogenous.) The crystallinity of each sample was further confirmed by powder X-ray diffraction. The ^{31}P NMR studies involved conducting chemical shift anisotropy (CSA) tensor measurements using a sheared Phase Adjustment of Spinning Sidebands (PASS) experiment and J-coupling measurements using the Phase Incremented Echo-Train Acquisition (PIETA) pulse sequence. The CSA measurements for the crystalline pyrophosphate sites had an anisotropy (ζ) of 66 to 82 ppm and an asymmetry (η) of 0.15 to 0.40 which also seem to show little correlation with the type of metal cation in the salt (sample PASS spectrum shown in figure 2.) The measured J-coupling constants ranged from 17.5 to 25.8 Hz for the crystalline samples as compared to a larger 0 to 25 Hz range for amorphous samples (sample J-coupling spectrum shown in figure 3.) All of these crystalline pyrophosphate samples had a bent geometry for the P–O–P linkage. These results imply that previously studied amorphous samples have a much wider range of bond-angles linking the pyrophosphate tetrahedra.

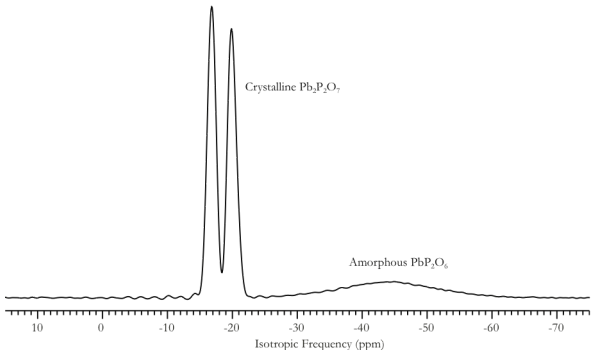

Figure 1. MAS spectrum of $Pb_2P_2O_7$ synthesized using the high temperature approach. The crystal structure has two distinct phosphorus atoms in the pyrophosphate anions giving rise to the sharp peaks at –20 ppm. Broad peak at –42 ppm is an amorphous impurity produced in the slow cooled sample.

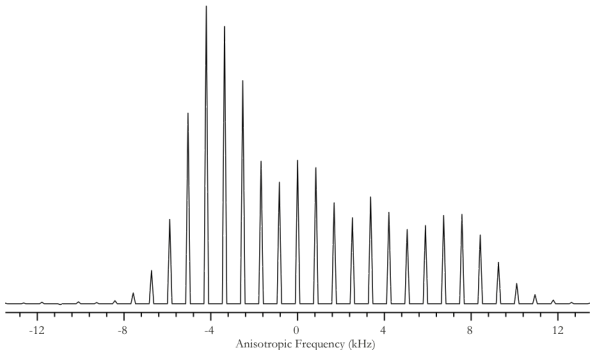

Figure 2. Anisotropic PASS spectrum of $Pb_2P_2O_7$ synthesized using the high temperature approach. Chemical shift tensor for site at –17 ppm was simulated giving a ζ of 75.7 ppm and η of 0.29, consistent with other crystalline pyrophosphate sites.

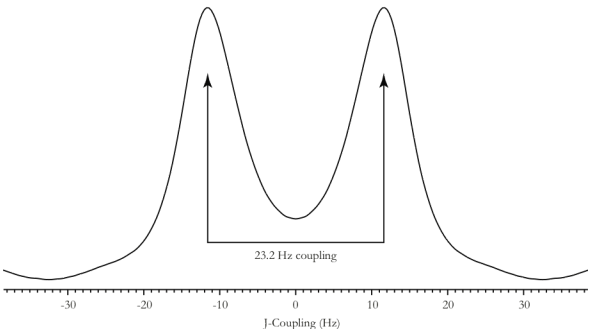

Figure 3. J-Coupling spectrum of $Pb_2P_2O_7$ synthesized using the high temperature approach. The doublet is split by 23.2 Hz with relatively narrow peaks indicating a highly crystalline pyrophosphate anionic geometry.