

# Studies of Distributional Effects in Alkaline Phosphate Glasses

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## Abstract

Crystalline and amorphous compounds differ primarily in two ways. First, amorphous samples lack long-range order and second, they often lack well defined local bonding geometries. These two differences must be solely responsible for the immense diversity of properties found in amorphous systems. We propose to study how specific *macroscopic* physical properties of phosphate based glasses are related to the bond-angle and chain-length *distributions* found in these glasses. Intrinsically this means looking beyond the properties of *average* bonding environments and instead describing the *distributions* of bonding environments. We propose to measure medium-range structure in these glasses with solid-state nuclear magnetic resonance (NMR) techniques. NMR will provide chemical shift tensors which will be converted into structural information using correlations derived by combining experiments (1, 2) and *ab initio* calculations. The techniques of magic-angle spinning (MAS) and magic-angle turning (MAT) will be used to extract chemical shift tensors from amorphous samples with the  $x\text{Na}_2\text{O}\cdot y\text{K}_2\text{O}\cdot \text{P}_2\text{O}_5$  composition (ranging from metaphosphates to orthophosphates). We will examine the effect of composition on the derived bond-angle distributions and attempt to establish correlations between these distributions and the measured ionic conductivity in these glasses. These experiments represent *new applications* of existing techniques to address fundamental questions in a basic class of materials. The proposed research will involve undergraduate research assistants who will work on *all* aspects of this research, including running NMR experiments and interpreting the results, providing a vital element in their professional education as chemists.

## Introduction

Glasses are technologically important in an *enormous* range of applications because of their diverse optical, transport and structural properties. These applications are primarily determined by the physical properties of each glass, which are in turn governed by the composition and preparation of that glass (3). Phosphate glasses may function as photoconductors, solid electrolytes and low-frequency waveguides with the element phosphorus playing the important role of glass former in these materials (4, 5). Those properties unique to glasses (as opposed to crystalline compounds) *must* result from the combined effect of the absence of long range order and the distributions of local bonding environments. For instance, all Si-O-Si bond angles in  $\alpha$ -quartz are  $143^\circ$  while in vitreous  $\text{SiO}_2$  they ranges from  $120^\circ$  to  $180^\circ$  with a peak near  $144^\circ$ ; both compounds have similar “average” values but the properties are markedly different (5) (i.e.  $\alpha$ -quartz has density of 2.65 g/mL while vitreous silica is 2.21 g/mL). We will use NMR as the tool to probe these sorts of differences.

In fact the use of NMR to study glasses has grown substantially in the last decade (6). In particular,  $^{31}\text{P}$  magic-angle spinning (MAS) NMR has proven quite effective in these systems (7, 8, 9, 10) because of its moderate dipolar coupling, large isotropic chemical shift range and large chemical shift anisotropies. While historically MAS has been used to study phosphate glasses, new NMR techniques such as DAS (11) and MAT (12, 13) can provide extended information about the local bonding distributions in  $^{31}\text{P}$  containing systems. The proposed research will use these recently developed 2D experiments (MAT in particular) to give significant improvements in the understanding of glass structure. The previous application of these sorts of 2D experiments, such as dynamic-angle spinning (14), have shown enormous potential for the study of glasses (11, 15).

The focus of our study will be on short and medium range structure present in phosphate glasses. Other than NMR, structurally sensitive experiments are somewhat limited when applied to amorphous materials. NMR, however, is a localized technique that has the capacity to probe the microscopic environment at each individual site in an amorphous material. We will convert the measured NMR parameters into structural information (i.e. bond-angle, ring-size or chain-length distributions) using *ab initio* calculations (derived from GAUSSIAN94). Note that this process is partially underdetermined and in reality there will be multiple bonding scenarios which may produce similar NMR spectra. We hope to offer data which can be used to strengthen some of these models and discount others. Ultimately we will correlate this structural information with chemical composition, sample preparation and eventually bulk physical properties. Additionally, the information would be invaluable to help test, clarify and improve existing molecular modeling and dynamics calculations.

## Experimental

We intend to study alkaline phosphate glasses in the  $x\text{Na}_2\text{O}\cdot y\text{K}_2\text{O}\cdot \text{P}_2\text{O}_5$  series (ranging from metaphosphates to orthophosphates) using a two-fold approach. First, the glasses will be prepared and studied with modern NMR spectroscopic techniques (MAS, MAT). Second, the results will be compared to simulated NMR parameters from a variety of model compounds using *ab initio* quantum calculations (GAUSSIAN94). Bringing the computer simulations together with the experimental data will allow us to refine existing models and search for correlations between the phosphate bonding environments and ionic conductivity effects.

## Synthesis

The glasses will be synthesized at Berea from high purity materials using standard techniques (5, 8, 16, 17). This involves heating the finely ground mixtures of  $\text{P}_2\text{O}_5$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  significantly above the melting temperatures (usually around  $1000^\circ\text{C}$ ) and cooling in a controlled fashion. For samples where the product, such as high  $\text{P}_2\text{O}_5$  content glasses, may vaporize and change sample composition, glasses may be synthesized in inert atmosphere in a glove box or in

sealed tubes. Sample composition will be analyzed using both an atomic absorption spectrometer (monitoring both alkali metal and phosphorus concentrations) as well as a gravimetric method (precipitating out  $\text{Ba}_3(\text{PO}_4)_2$  or  $\text{AlPO}_4$ ). Amorphous and crystalline alkaline phosphate samples (of the previously mentioned compositions) *were prepared in this fashion already* by undergraduate research assistants at Berea College during the summer of 1994 and short term 1996 (see figure 1 below). A variety of quenching techniques (air cooled, splat cooled, liquid cooled) were explored and we will systematically evaluate how these different approaches affect observed microscopic parameters and determine if this is correlated with the macroscopic properties. Phase and crystallinity information will be determined with powder X-ray diffraction (conducted at the Ohio State University, OSU).

### MAS and MAT NMR

These NMR experiments will be carried out primarily at the University of Kentucky (UK) using a MAS probe purchased this spring and ultimately at Berea College once we have suitable instrumentation (currently this is budgeted for FY1999). In addition, some of this work will continue to be conducted at OSU in the laboratory of Dr. P. J. Grandinetti as this has proven to be a valuable collaboration in this area. MAS is a NMR experiment which gives high resolution isotropic spectra for  $^{31}\text{P}$  sites by averaging the chemical shift anisotropy and homonuclear dipolar in-

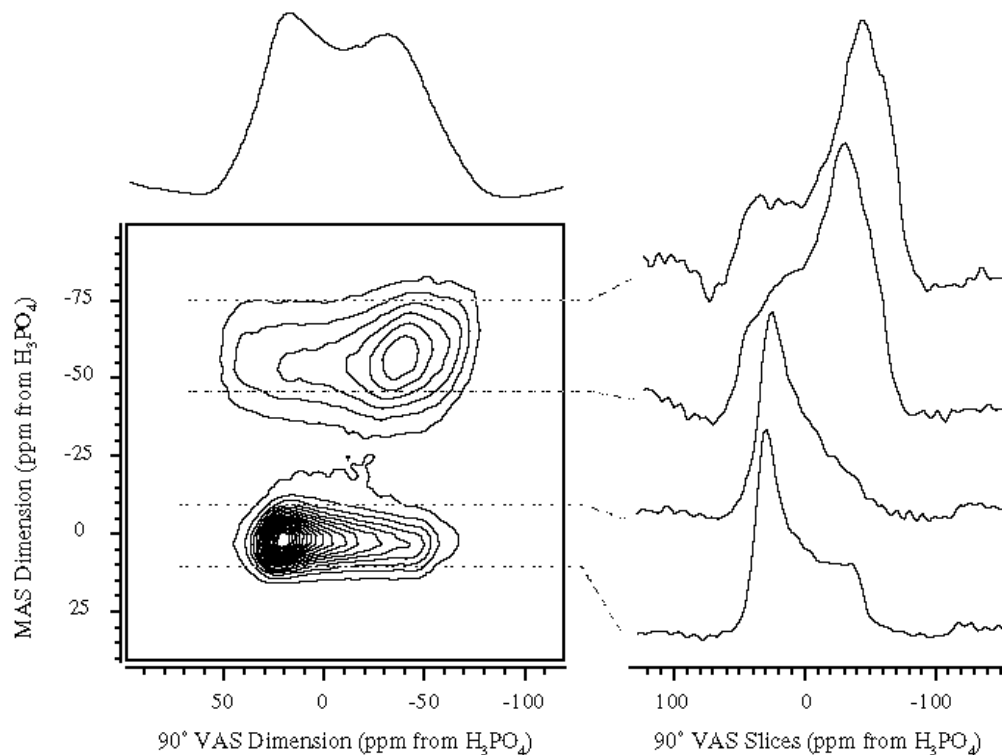


Figure 1.  $90^\circ$  - MAS Correlation Spectrum of  $5\text{Na}_2\text{O}\cdot 4\text{P}_2\text{O}_5$  Glass.  $90^\circ$  VAS Slices taken through the MAS dimension are shown on the right as well as a total  $90^\circ$  projection. Notice that the singularity positions in these patterns do not shift uniformly across a  $\text{Q}^2$  ( $-50$  ppm) or  $\text{Q}^1$  ( $0$  ppm) site.

teractions. These types of spectra are useful because the isotropic chemical shift is related directly to coordination and bonding environment (9). Additional two-dimensional experiments (MAT) will be performed that correlate isotropic shifts with anisotropic lineshapes. MAT is an NMR experiment in which a sample is effectively moved through three orthogonal directions providing anisotropic averaging using a conventional MAS probe (12, 13). This method is *superior* to similar correlation experiments, since there will be little dipolar broadening (a major problem for  $^{31}\text{P}$ ) in the either dimension because the sample spins about the magic-angle at rates of 1 to 5 kHz (slow enough to still generate a large number of spinning sidebands). The data collected in this fashion will also be pure-absorptive phase without necessitating unusual sample reorientation methods, in contrast to other techniques such as VACSYS (18). From our work at OSU it appears that DAS may also be used to gain anisotropic information in a MAS-VAS correlation experiment. Currently, efforts are underway to complete analysis of a DAS data set (see figure 1 above) from a  $5\text{Na}_2\text{O}\cdot 4\text{P}_2\text{O}_5$  glass sample. This glass, made at Berea and run on a 400MHz spectrometer at OSU during January of 1996 shows a clear distribution of CSA tensors. The critical feature in this spectrum is that the CSA patterns change as you go across each site which means that there is additional information about the local geometries at different sites within a general Q-species class not available from 1D MAS spectra alone.

### Computer Calculations

In all of the proposed experiments we utilize computers to simulate the NMR spectra and to interpret parameters extracted from the data. New desktop workstations make the simulation of NMR lineshapes and calculation of chemical shift tensors from *ab initio* molecular orbital programs quite feasible at Berea College; in fact this summer we will be setting up a UNIX workstation with this software. The computer programs needed to convert the NMR powder pattern lineshapes into CSA tensors already are running on local computers and have been tested on portions of the previously mentioned  $5\text{Na}_2\text{O}\cdot 4\text{P}_2\text{O}_5$  glass data set. The distribution of tensors extracted will be compared with small phosphate clusters as models using GAUSSIAN94 to do *ab initio* simulations. Specifically, we will explore the effect of changing the individual O-P-O bond angles and lengths as well as the effect of chain length on the chemical shift tensor using  $\text{PO}_4^{3-}$ ,  $\text{P}_2\text{O}_7^{4-}$  and  $\text{P}_3\text{O}_{10}^{5-}$  fragments with appropriately located alkali metals for charge balance. Extensive crystalline chemical shift tensor data exists which will be used to help refine the basis set requirements and minimize computational complexity (thereby allowing *ab initio* studies of even larger molecular fragments). Undergraduate research assistants can make immediate contributions to these projects by becoming involved in computer programming without extensive NMR experience.

## Interpretation

To some degree, the large database of  $^{31}\text{P}$  chemical shift information which already exists will allow us to quickly make some interpretation of CSA parameters in terms of distributions of bond lengths and angles. By combining computer simulations with experimental data, we will be able to interpret the NMR spectra of glasses in terms of bond angle distributions with greater reliability and accuracy. We will continue examining how macroscopic properties depend on the observed microscopic *distributions* (as opposed to *averages*). In the future, other NMR active nuclei (i.e.,  $^{29}\text{Si}$ ,  $^{23}\text{Na}$  or  $^7\text{Li}$ ) will be studied using both the traditional solid-state NMR technique of MAS and the new triple-quantum filtered MAS (19) and MAT experiments for structural characterization of a sample.

## Conclusions

In this study, we will continue to investigate the structural order and disorder in a variety of glasses using NMR as a microscopic probe. Specifically, we hope to obtain quantitative information regarding distributions of bond angles and other structural features which will be compared with *macroscopic* properties (4). It is anticipated that the understanding of the formation of short and medium-range order on a *microscopic* level will help to describe these *macroscopic* properties. In particular, we will address how this microscopic structure affects the mechanism of ionic conduction and evaluate why specific chemical changes lead to reduction or enhancement of this conductivity. This structural information will be an invaluable aid when engineering glasses to achieve more predictable and possibly useful physical properties (for example in looking for improvements in the ion conductors used in fuel cells and batteries).

This research project may be successfully completed by undergraduate students here at Berea and each portion of this project is relatively straightforward to perform and can lead to *significant* results. While most of this work will be conducted in the chemistry department at Berea College, experiments requiring equipment we do not have will be carried out at UK and OSU, giving the undergraduates the opportunity to be involved in a large scale research environment (as was done the summer of 1994 and short term 1995). Overall, this research should not be in direct competition with any of the major research labs and will in fact be in collaboration with the Grandinetti group at OSU (see attached letter).

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