

I propose to study the connection between the microscopic structures, such as bond angle distributions, found in alkali modified metaphosphate glasses and their overall physical properties, such as ionic conductivity. The microscopic structures, both short and medium range, will be examined using modern solid state nuclear magnetic resonance (NMR) techniques. NMR provides nuclear spin parameters (i.e., chemical shift tensors) which can be converted into structural properties using correlations derived from both experiments and *ab initio* calculations. This will be accomplished by combining previously developed magic-angle spinning and new two-dimensional magic-angle hopping techniques with computer simulations.

Introduction

Glasses are technologically important in an enormous range of applications because of their diverse optical, transport and structural properties. The type of application is primarily determined by the physical properties of each glass which in turn are governed by the composition and preparation of that glass.¹ 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. In the past thirty years the use of NMR to study glasses has grown substantially.² In particular, ³¹P MAS NMR has proven quite effective in these systems³⁻⁵ because of its moderate dipolar coupling, large isotropic chemical shift range and large chemical shift anisotropies. Until only recently NMR has been utilized in rather simplistic one-dimensional MAS experiments, which yield limited information. While historically MAS has been used to study glasses, new NMR techniques such as MAH⁶ can provide penetrating information about the local bonding in ³¹P containing systems. The proposed research will use these recently developed 2D experiments (MAH in particular) to give significant improvements in the understanding of glass structure. The previous application of these sorts of experiments, such as dynamic-angle spinning,⁷ have shown enormous potential for the study of glasses.⁸

The types of questions we will address concern short and medium range structure present in phosphate glasses. Other than NMR, structurally sensitive experiments are somewhat limited in application to amorphous materials. X-ray diffraction relies on the existence of long range translational order and x-ray scattering involves deconvoluting multiple atom-pair correlation functions. Other spectroscopic techniques rarely give significant insight into local environmental differences. NMR, however, is a localized technique that has the capacity to probe the microscopic environment at each individual site in an amorphous material. We hope to convert these measured NMR parameters into structural information (i.e., bond-angle, ring-size or chain-length distributions) using *ab initio* calculations. This structural information will be correlated with both chemical composition and sample preparation, and ultimately with physical properties.

Experimental

Initially, we intend to study phosphate (P₂O₅) based glasses and their alkali metal network modifications. To gain a better understanding of the local and medium range structures present in these glass systems, we will also study a number of crystalline systems of similar composition which will provide an empirical basis for the interpretation of NMR data on glasses. The large database of ³¹P chemical shift information which already exists will allow us to quickly direct our research efforts to the more interesting amorphous samples. All crystalline and glassy samples will be synthesized from high purity materials using standard techniques.⁹ This involves heating the finely ground mixtures significantly above the melting temperatures

(usually about 1000° C) and cooling in a controlled fashion. For samples where the starting materials, such as P₂O₅, may vaporize and change sample composition, a vacuum sealed approach will be used. Amorphous and crystalline alkaline metaphosphate (Li_xNa_yK_{1-x-y}PO₃) samples were prepared in this fashion already by undergraduate research assistants at Berea College during the summer of 1994. A variety of quenching techniques were explored and a “splat” cooling technique (pouring the liquid sample onto a cold copper plate and quickly pressing flat with a second plate) proved most effective. Powder X-ray diffraction was used to determine both phase and crystallinity information and NMR experiments were conducted at the Ohio State University (OSU) looking at the ³¹P nuclei in these samples. In the future, other NMR active nuclei (i.e., ²⁹Si, ²³Na or ⁷Li) will be studied using both the traditional solid-state NMR technique of MAS and the new two-dimensional MAH experiment for structural characterization of a sample. These NMR experiments will be carried out at both Berea College using a MAS probe we plan to build and at OSU in the laboratory of Dr. P. J. Grandinetti. Finally, the interpretation of the NMR parameters will be aided using a variety of simulation and ab initio calculation programs which will be performed on the computers at Berea College. In all cases, undergraduate research assistants will be involved in the *preparation* and *characterization* (including running NMR experiments) of samples as well as the simulation of spectra.

MAS is a NMR experiment which gives high resolution isotropic spectra for spin $\frac{1}{2}$ systems, such as ³¹P and ²⁹Si, by averaging the chemical shift anisotropy interaction. These types of spectra are important because the isotropic chemical shift may often be related directly to coordination and bonding environment.¹⁰ MAH is a two-dimensional NMR experiment in which a sample is moved through three orthogonal directions providing anisotropic averaging using a conventional MAS probe.^{11,12} This produces sideband free isotropic spectra correlated with anisotropic spinning sideband patterns, which will work well for ³¹P where the chemical shift anisotropies are quite large. This method is *superior* to similar correlation experiments, since there will be little dipolar broadening in the either dimension since the sample may be continuously spun about the magic-angle at rates of 1 to 5 kHz and 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 most of the other techniques (i.e. VACSYS,¹³ DAS⁷). From our work at OSU it appears that for particularly favorable systems, MAS *alone* may be used to gain anisotropic information. We have observed that the MAS spectra of the metaphosphates are inhomogeneously broadened by a distribution of chemical shifts. Therefore, a modified Herzfeld and Berger spinning sideband analysis¹⁴ of a single 1D MAS spectrum can generate complete tensor distribution information for a material.

All the proposed experiments rely on the creation and application of computer code to simulate the NMR spectra and extracted parameters. New desktop workstations makes the simulation of NMR lineshapes and calculation of electric field gradients and chemical shift information from *ab initio* molecular orbital programs quite feasible at Berea College. In addition, undergraduate research assistants can make immediate contributions to these projects by becoming involved in computer programming without extensive NMR experience. By combining computer simulations with experimental data, we will be able to interpret the NMR spectra of glasses with greater reliability and accuracy. This is important in the quantization of structural parameters in glasses from chemical shift tensors. Specifically, we will explore the effect of changing the O–P–O bond angles or the effect of chain length on the chemical shift tensor using *ab initio* calculations on small molecular fragments of alkali rich metaphosphates.

Conclusions

We will investigate the structural order and disorder in a variety of glasses using NMR as a probe at the microscopic level. Ultimately the understanding of the formation of short and medium range order on a *microscopic* level will help to describe *macroscopic* properties. This structural information will be an invaluable aid when engineering glasses to achieve more predictable physical properties.

Additionally, these research projects will be of the type which may be successfully completed by an undergraduate student. Each element in this research 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 larger nearby universities, giving the undergraduates the opportunity to be involved in a large scale research environment. This would involve taking students to a school such as OSU (as was done the summer of 1994) for part of the summer research program to do experiments such as DTA, TGA, XRD and high-field NMR. 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). Finally, the equipment purchased for this research will be used to supplement the physical chemistry and instrumental analysis laboratories at Berea College by bringing FT NMR within the grasp of our students. Specifically, the introduction of basic solid state NMR experiments at the undergraduate level would be highly profitable for students bound for graduate school.

References

- 1 S. R. Elliott, *Physics of Amorphous Materials*, 2nd ed. (Longman Scientific & Technical, Essex, England, 1990).
- 2 H. Eckert, *Progress in Magnetic Resonance Spectroscopy* 24, 159-293 (1992).
- 3 D. Lathrop and H. Eckert, *Journal of the American Chemical Society* 111, 3536-3541 (1989).
- 4 S. Prabhakar, K. J. Rao, and C. N. R. Rao, *Chemical Physics Letters* 139, 96-102 (1987).
- 5 G. Turner, K. A. Smith, R. J. Kirkpatrick, and E. Oldfield, *Journal of Magnetic Resonance* 70, 408-415 (1986).
- 6 A. Bax, N. M. Szeverenyi, and G. E. Maciel, *Journal of Magnetic Resonance* 52, 147-152 (1983).
- 7 I. Farnan, P. J. Grandinetti, J. H. Baltisberger, J. F. Stebbins, U. Werner, M. A. Eastman, and A. Pines, *Nature* 358, 31-35 (1992).
- 8 J. W. Zwanziger, K. K. Olsen, and S. L. Tagg, *Physical Review B - Condensed Matter* 47, 14618-14621 (1993).
- 9 J. H. Kennedy and Z. M. Zhang, *Solid State Ionics* 30, 726 (1988).
- 10 R. K. Sato, R. J. Kirkpatrick, and R. K. Brow, *Journal of Non-Crystalline Solids* 143, 257-264 (1992).
- 11 Z. Gan, *Journal of the American Chemical Society* 114, 8307-8309 (1992).
- 12 S. L. Gann, J. H. Baltisberger, and A. Pines, *Chemical Physics Letters* 210, 405-410 (1993).
- 13 L. Frydman, G. C. Chingas, Y. K. Lee, P. J. Grandinetti, M. A. Eastman, G. A. Barrall, and A. Pines, *Journal of Chemical Physics* 97, 4800-4808 (1992).
- 14 J. Herzfeld and A. E. Berger, *Journal of Chemical Physics* 73, 6021-6030 (1980).