

The Study of Medium-Range Order in Phosphate and Silicate Glasses

Jay Baltisberger – Berea College

Camille and Henry Dreyfus Foundation Start-up Grant Proposal

Abstract

I plan to investigate the short and medium range structures present in a variety of technologically important phosphate, phosphosilicate, and phosphorus chalcogenide glasses with and without alkali cation modification 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. These experiments include new two-dimensional correlation experiments which have never been applied to these glass systems and can provide much more detailed information than simple one-dimensional experiments used previously.

1.0 Introduction

Glasses are technologically important in a wide range of applications because of their unique 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 glass¹. Non-oxide chalcogenide glasses appear in photoconductors, solid electrolytes and low-frequency waveguides. The element phosphorus plays the important role of glass former in many of these materials. In the past thirty years the use of nuclear magnetic resonance to study glasses has grown substantially². In particular, both static and magic-angle spinning (MAS) ³¹P NMR has proven quite effective in these systems³⁻⁷ because of its strong dipolar coupling, large isotropic chemical shift range and large chemical shift anisotropies. For example, the sizes of clusters and types of primary structural units in the binary P-Se system have been extensively studied with NMR experiments.

A second type of glasses are the silicates, phosphates and phosphosilicates. These types of oxide glasses of commercial and geological significance, have been extensively studied with ²⁹Si NMR⁸⁻¹⁰. While historically MAS^{11,12} has been used to study glasses, new NMR techniques such as magic-angle hopping (MAH)¹³ can provide additional information about the local bonding in ³¹P, ²⁹Si, ²⁰⁷Pb and other spin $\frac{1}{2}$ systems. An example of this is the determination of bond angles and local geometries in silicate glasses with ²⁹Si NMR.

The types of questions I hope to address concern short and medium range structure present in these glasses. Experiments other than NMR are often limited in application to amorphous materials. X-ray diffraction relies on the existence of long range translational order (absent in glasses) and x-ray scattering involves deconvoluting multi-atomic correlation functions. Both of these techniques are extremely limited in application to glasses involving more than two atom types. Other spectroscopic techniques such as UV and IR spectroscopy are bulk techniques and do not give significant insight into local environmental differences. NMR, however, is a localized technique which has the capacity to probe local environments at each site in an amorphous material. I hope to convert measured NMR parameters into structural information (i.e. bond angle distributions) using ab initio calculations.

2.0 Experimental

I intend to study phosphorus chalcogenide, phosphate and silicate glasses such as PSe, P₂S₅, P₂O₅ and SiO₂ and their alkali metal network modifications and combinations. To gain a better understanding of the local and medium range structures present in 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. Both crystalline and glassy samples will be synthesized from high purity materials using standard techniques¹⁴. This involves heating the finely ground mixtures above the melting temperatures (often greater than 1000° C) and cooling in a rapid controlled fashion. Each NMR active nucleus will be studied using both the traditional solid-state NMR technique of MAS and the new two-dimensional MAH experiment to achieve high resolution spectra and static NMR for rapid characterization of a sample. Finally, the interpretation of the measured NMR parameters will be aided using a variety of simulation and ab initio calculation programs which may be performed on a small workstation. In all cases, undergraduate research assistants will be involved in the preparation and characterization of samples as well as the simulation of NMR spectra.

2.1 MAS and MAH NMR on Phosphate and Silicate Glasses

MAS is a one-dimensional NMR experiment which will give high resolution isotropic spectra of spin $\frac{1}{2}$ systems, such as ³¹P and ²⁹Si, by averaging the chemical shift anisotropy interaction. This is achieved by spinning the sample about an axis inclined 54.74° from the static magnetic field. These types of spectra are important because the isotropic chemical shift may often be related directly to coordination and bonding environment. For example, in ²⁹Si NMR a number of experiments have been performed which relate both the types of oxygen coordination at an individual Si site and the Si-O-Si bond angles to the measured isotropic chemical shifts. By performing multiple pulse experiments in conjunction with sample rotation, a variety of two-dimensional experiments will be performed that correlate isotropic shifts with isotropic shifts (MAS)¹⁵ and isotropic shifts with anisotropic lineshapes (MAS, MAH)^{16,17}. These experiments are performed by collecting a set of one-dimensional free induction decays in which at least one of the evolution time periods prior to data collection is incremented for each experiment. The two-dimensional Fourier transform of this type of data gives additional information by correlating evolution frequencies in two dimensions. MAH is a new two-dimensional NMR experiment in which a static sample is moved sequentially through three orthogonal directions providing anisotropic averaging. This may be performed using a conventional MAS probe spinning at very slow speeds¹⁷. This experiment produces sideband free isotropic spectra correlated with anisotropically broadened powder patterns which will work well for ³¹P where the chemical shift anisotropies are quite large. The comparison of this data with the chemical shift tensors from ab initio calculations will aid in quantifying site distributions.

2.2 Computer Simulations and Calculations

All the proposed experiments rely on the creation and application of computer code to simulate the NMR spectra and extracted parameters. The advent of fast 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. In addition, undergraduate research assistants can make immediate contributions to these projects by becoming involved in computer programming without extensive prior NMR experience. By combining computer simulation with experimental data,

I will be able to interpret the NMR spectra of glasses with greater reliability and accuracy. This is important in the quantization of structural parameters such as a site symmetry distribution in a phosphate glass from chemical shift tensors.

3.0 Conclusions

I 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 and easy to perform and can lead to significant results. Also, some research 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 two or three students to a school such as the University of Kentucky or Ohio State University for three or four weeks of the ten to twelve week summer research program to do experiments which cannot be performed at a small school like Berea College. Finally, the equipment purchased for this research will be used to supplement the physical and analytical chemistry laboratories at Berea College. Specifically, the introduction of both basic imaging and solid state NMR experiments at an early level would be highly profitable for undergraduates bound for graduate school. At Berea I would be teaching both physical and analytical chemistry upper division courses as well as some general chemistry courses for freshmen.

4.0 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 J. H. Kennedy and Z. M. Zhang, *Journal of the Electrochemical Society* **136**, 2441-2443 (1989).
- 7 J. P. Malugani and G. Robert, *Solid State Ionics* **1**, 519 (1980).
- 8 J. B. Murdoch, J. F. Stebbins, and I. E. Carmichael, *American Mineralogist* **70**, 332 (1985).
- 9 B. D. Mosel, W. Müller-Warmuth, and H. Dutz, *Physics and Chemistry of Glasses* **15**, 154 (1974).
- 10 R. F. Pettifer, R. Dupree, I. Farnan, and U. Sternberg, *Journal of Non-Crystalline Solids* **106**, 408-412 (1988).
- 11 I. J. Lowe, *Physical Review Letters* **2**, 285 (1959).
- 12 E. R. Andrew, A. Bradbury, and R. G. Eades, *Nature* **183**, 1802-1803 (1959).

- 13 A. Bax, N. M. Szeverenyi, and G. E. Maciel, *Journal of Magnetic Resonance* **52**, 147-152 (1983).
- 14 J. H. Kennedy and Z. M. Zhang, *Solid State Ionics* **30**, 726 (1988).
- 15 C. A. Fyfe, H. Grondey, Y. Feng, and G. T. Kokotailo, *Journal of the American Chemical Society* **112**, 8812-8820 (1990).
- 16 R. Tycko, G. Dabbagh, and P. A. Mirau, *Journal of Magnetic Resonance* **85**, 265-274 (1989).
- 17 Z. Gan, *Journal of the American Chemical Society* **114**, 8307-8309 (1992).

Jay Baltisberger

The following is a tentative description of the use of research funding from Camille and Henry Dreyfus Foundation and other funding sources.

I would like to use one or more grants to purchase the following equipment over a number of years (ranked in order of importance). Berea College has already agreed to provide an initial \$10,000 to \$12,000 startup funding. In addition, the college has been awarded a Kresge Science Initiative Grant, which will provide support funding over the years.

1. Upgrade for existing JEOL FX90Q spectrometer to Tecmag LEO-J acquisition system (\$10,000 to \$20,000).
2. High power broadband X-channel RF amplifier (10-200 MHz, 300 W, \$6000)
3. High power tuned H-channel RF amplifier (90 or 180 MHz, 300 W, \$4000)
4. Spinning assembly for a magic-angle spinning probe (\$4500)
5. High temperature (>1500°C) oven (\$1000)
6. Desktop computer workstation for simulations and ab initio calculations (\$8,000)
7. High-frequency oscilloscope and frequency sweeper (\$6000)

Additionally, I would like to use some grant money to fund my summer salary as well as two or three undergraduate research assistants. Included would be funding for travel (including the undergraduates) for three or four weeks out of twelve to Ohio State University or Indiana University to work with either Prof. P.J. Grandinetti or Dr. J.W. Zwanziger respectively. This travel would be especially important in the first few summers while I am acquiring the equipment needed to do this work at Berea. (\$15,000 total per summer including undergraduate salaries and travel)