Final Report

University of Wyoming

Laramie, WY 82071

Department of Chemistry

Application of Pulsed Neutron Scattering to the Structural and Dynamic Characterization of Amorphous Solids and Associated Phase Transitions: A Partnership between Argonne National Laboratory and the University of Wyoming.

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SUMMARY

The successful creation of a focused research group bringing together physicists and chemists from the University of Wyoming and Argonne National Laboratory has allowing unique interdisciplinary research for scientists and students. The current collaborators on the project include Dr. David Price from Argonne National Laboratory and Prof. Jeff Yarger from the University of Wyoming as well as several other scientists including Dr. Chris Benmore (benmore@anl.gov) and Dr. Alexander Kolesnikov (akolesnikov@anl.gov). In the past three years of funding, we have partially supported one graduate student (Kristina Lantzky, Univ. Wyoming) and fully supported one postdoctoral fellow (Dr. Sajatha Sampath, ssampath@pns.anl.gov).

From the results obtaining in our three years of funding from the Department of Energy, we have published six scientific articles and are currently working on several others. Copies of this publication as well as recently submitted publications will be provided with this final report.

TECHNICAL REPORT

❁ DENSIFIED GLASSES:

The effect of hydrostatic pressure on the structure of glasses is not well understood. There is extensive evidence now indicating that glasses undergo structural transformation upon application of pressure. These transformations are usually evidenced by changes in density, sound velocity, and structural changes from diffraction measurements (x-ray and neutron). In vitreous GeO₂, a change in Ge-coordination from 4-6 is evidenced on the application of pressure. The coordination change reverts back to 4 on releasing the pressure indicating that the structural transformation is reversible with pressure. But a shift towards higher Q (inverse space) of the first sharp diffraction peak (FSDP) on the pressure compacted v-SiO₂ and v-GeO₂ suggests that application of pressure has both reversible and irreversible components such that on the release of pressure, the glass remains in a permanently compacted state.

DOE Patent Clearance Granted

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Figure 1- Schematic of GeO_2 Glass Molecular Structure

We have measured the structure factor $S(Q)$ for densified $v\text{-GeO}_2$ (10 GPa) by neutron diffraction at the Glasses liquids and amorphous diffractometer (GLAD) at IPNS-ANL. The radial distribution function was obtained by Fourier transforming of the scattering function - $S(Q)$. The main results obtained from this study were that the intermediate range order was reduced on densification. This implied that the inter-tetrahedral distance has shortened. There was a slight increase in the Ge-O short-range order length. But the Ge-coordination of the densified glass was found to retain its original value of 4. To arrive at the exact structure, knowledge of all the partial pair-correlations (Ge-O, Ge-Ge, O-O) is required. This could either be done neutron diffraction by isotopic substitution, wherein $S(Q)$ is measured with different isotopes of either Ge or O and their difference is taken to give the partial structure factors. But this is a rather expensive technique.

Combination of neutron diffraction and high energy X-ray diffraction - Third generation synchrotron sources provide a very intense and high energy flux, which facilitates spanning a larger Q range, and in turn a higher resolution for the real space correlation lengths. We measured the $S(Q)$ of densified GeO_2 glass (same sample as used for neutron diffraction) in the high-energy (110 KeV) beamline 11ID-C, BESSERC-CAT at the Advanced Photon source in the Argonne National Laboratory (proposal to available beam-time was written). X-ray scattering is dominated by the Ge correlations and the neutron scattering by the O correlations. Hence by combining the information from both X-ray and neutron diffraction on the same sample, and the fact that both the data being in the same Q -range, by careful normalization and taking the first order difference, we have successfully been able to get all the three partial pair-correlation. To the best of our knowledge, this is the first study wherein all the full structure of a densified glass has been determined experimentally. We have interpreting the results and published the results in *Physical Review Letters*.

✿ STRUCTURAL INVESTIGATION OF AMORPHOUS BeH_2 AND BeD_2

Beryllium hydride is an incredible interesting system because of its relative simplicity. Besides being a relatively simple 2-component system from the fundamental science aspect, it also has potential applications in nuclear materials technology and high-energy fuel technology. It could also be a potential isomorphic system with water, which has recently been shown to exhibit interesting properties in the glassy state. The determination of partial structure factors

using neutron diffraction with isotopic substitution (NDIS) relies on the subtraction of experimental data sets for two samples whose only difference is the isotopic identity at a known atomic site in the sample – the main assumption here being isotopic substitution leaves the atomic level structure of the sample unchanged. *This assumption turned out NOT to be true for Beryllium Hydride!*

Synthesizing beryllium hydride based samples in bulk amounts needed for neutron experiments (typically 3-4 grams) are very difficult (synthesized by graduate student K. Lantzky in Prof. Jeff Yarger's Lab. in the University of Wyoming). Secondly, the materials having a high hydrogen content results in a substantial contribution from inelastic scattering in the data, the analysis of which makes it very complicated. In this regard, we have performed preliminary x-ray and neutron diffraction experiments on BeH_2 and BeD_2 at ANL. These measurements showed a very unexpected structural quantum isotope effect. In fact, it is the largest quantum isotope effect ever seen. We immediately published these results in the *Journal of Chemical Physics* and we are currently working with a new postdoctoral fellow, Qiang Mei, to further characterize this unusual material.

✳ STRUCTURAL INVESTIGATION OF CALCIUM ALUMINATE GLASSES

Liquids formed from binary $\text{CaO-Al}_2\text{O}_3$ materials can be vitrified to form hard, transparent, colorless glasses. The glasses exhibit infrared transmission to *ca.* 5500 nm and are potentially useful as a laser host and infrared optical material. Many crystalline calcium aluminate phases are of interest from the geological standpoint, and are common components of hydraulic cements.

Spallation neutron diffraction and high energy x-ray diffraction methods have been used to study $\text{CaO:Al}_2\text{O}_3$ glasses at the 64:36 eutectic and 50:50 mole % compositions. Containerless cooling of liquid droplets heated by a laser beam and suspended in an aerodynamic levitator produced the samples. Whilst both the neutron and x-ray data reveal

Figure 2 - The real space neutron $G_N(r)$ & x-ray $G_X(r)$ radial distribution functions for the $\text{CaO-Al}_2\text{O}_3$ eutectic (solid line) and equimolar glasses (dashed line).

The results show aluminum on average to be surrounded by 4.0 oxygen atoms at a distance of 1.76Å in CaAl_2O_4 but the Al-O coordination number increases to 4.8 at the eutectic composition. The two techniques have also been combined to reveal the local structure of the calcium atoms in the glass. In CaAl_2O_4 the Calcium is found on average to be surrounded by 5.6 oxygen atoms at a distance of 2.38Å. The Ca coordination decreases to 3.9 oxygen atoms at the eutectic composition. Corner sharing units with approximate ion-ion distances of Al-Al at 3.1Å, Ca-Al at 3.2Å and Ca-Ca at 3.5Å dominates the connectivity of the glass. The results are compared to previous studies near the eutectic composition made by splat quenching. The results indicate that whilst the equimolar glass is on average composed mainly of AlO_4 tetrahedra, the eutectic composition the glass is dominated by AlO_5 polyhedra. Moreover, the calcium coordination decreases from mainly CaO_6 to CaO_4 , although the Ca-O bond distance changes only slightly. This work has been published in the *Journal of Physics: Condensed Matter* (2003).

✿ STRUCTURAL INVESTIGATION OF MAGNESIUM SILICATE GLASSES

Glasses made from the magnesium silicate mineral enstatite (MgSiO_3) and forsterite (Mg_2SiO_4) and three intermediate compositions can be considered as analogues of quenched, end-member composition melts from the Earth and Lunar mantle. Combined neutron and x-ray diffraction data show an abrupt change in glass structure in a narrow compositional range. These structural change reflect a change from a glass characterized by corner shared SiO_4 tetrahedra and an approximately equal mixture of MgO_4 and MgO_5 polyhedra, to one in which the average coordination of magnesium by oxygen is increased to five. This result has major implications on the structural and dynamic properties of silicate material at depth in the earth. The results are currently being published in *Europhysics Letters*.

✿ IN-SITU HIGH-PRESSURE NEUTRON AND XRAY STUDIES

In collaboration with Dr. C.A. Tulk and M. Guthrie from the Oak Ridge National Laboratory and R. Hemley from the Geophysical Laboratory, we are now studying *in-situ* pressure-induced structural changes in network glasses. We have carried out preliminary measurements on v- GeO_2 utilizing a newly developed Moissanite cell, that can compress samples of $\sim 1 \text{ mm}^3$ to above 20 GPa with x rays. Dramatic changes in the $S(Q)$ functions are clearly visible through the 6 GPa transition where the Ge-coordination changes from 4-6. These data permit the characterization of both the local and intermediate-range structural processes that occur as GeO_2 densifies. Furthermore, this new technique is likely to become important in the study of many other systems, as it facilitates the *in-situ* measurement of the structure of amorphous materials under a new regime of extreme pressures. These initial results on v- GeO_2 have been submitted to *Nature* for publication.

✿ University of Wyoming and Argonne National Laboratory Collaboration:

This DOE EPSCoR grant was the catalysis for starting collaborations between J.L. Yarger's research group at the University of Wyoming and the Intense Pulsed Neutron Source (IPNS) group at Argonne National Laboratory (ANL). This collaboration has flourished under the

DOE EPSCoR program and continues to build momentum in the area of amorphous materials and high-pressure physics and chemistry. Recently, the Department of Defense (DOD) Army Research Office (ARO) awarded our collaboration additional funds to explore high-pressure metallic glass research and we continue to employ a joint postdoctoral student that works collaboratively between ANL and the University of Wyoming. Furthermore, many undergraduate and graduate students at the University of Wyoming have been able to travel to ANL and do experiments associated with this collaborative research effort. We hope to continue this collaboration for many years and hope to obtain future research support for both DOE and DOD. Lastly, we are also expanding this collaboration to include scientists at the Advanced Photon Source (APS) at Argonne. This will increase our characterization and high-pressure tools for characterization of amorphous solids.

The funding from DOE EPSCoR has led to numerous publications and presentations. A list of publications where the research results were accomplished as a direct result of DOE EPSCoR funding is listed in the last section of this report. The presentations are plenty and include talks at the National American Physical Society meetings and American Chemical Society meetings by D. Price, J. Yarger, and C. Benmore. Furthermore, the indirect results of DOE EPSCoR funded are incredible. This grant was responsible for (i) helping build a high-pressure neutron cell at IPNS, (ii) allowing domestic and international users at IPNS and APS to have assistance by Dr. Sampath, (iii) student participation in the Argonne Summer School program, (iv) allowing all scientists at the University of Wyoming (UW) to learn more about the facilities at Argonne because of presentation by Dr. Benmore and Dr. Teller at UW seminars, and (v) establishing a center for amorphous solids and materials research at UW.

✿ *Sujatha Sampath – Primary Research Associate:*

Dr. Sujatha Sampath was funded from this DOE EPSCoR grant for 2 1/2 years and was the primary researcher involved on this collaborative grant. Dr. Sampath worked full-time at Argonne National Laboratory and visited the University of Wyoming every semester for a minimum of two weeks. Dr. Sampath was partly responsible for maintaining user and equipment support at IPNS on the GLAD beamline. Having a full-time postdoctoral fellow at Argonne National Laboratory was of great benefit to Dr. Yarger's research group at the University of Wyoming. Students at Wyoming were able to collaborate with Dr. Sampath and she was able to assist students visiting Argonne with their experiments.

Dr. Sampath published several papers that are a direct result of the DOE EPSCoR grant funding. A complete list of publications that were a result of DOE EPSCoR funding is listed in the section below. Furthermore, Dr. Sampath attended and presented DOE related research at several conferences. These are listed below.

SEMINARS GIVEN BY DR. SAMPATH:

- (1) "*Rigidity Percolation in GexSe1-x Chalcogenide Glass Series - Structural And Thermal Study*" - May 2001' at the Dept. of Chemistry, University of Wyoming.
- (2) "*Structure determination of Glasses using neutron and high energy synchrotron X-ray diffraction*" - 30th Nov' 2001 at the Dept. of Physics, University of Wyoming.

- (3) "Recent developments in the structural determination of densified GeO_2 " – Dec 2001' - Group Meeting at the IPNS-ANL.
- (4) "Recent developments in the structural determination of Densified GeO_2 " - XIX Congress and General Assembly of the International Union of Crystallography - August 6 – 15, 2002, Geneva, Switzerland.

PUBLICATIONS

- [1] B.E. Schwickert, S. Kline, H. Zimmerman, K. Lantzky, and J.L. Yarger. "Early Stages of Glacial Clustering in Supercooled Triphenyl Phosphite." *Phys. Rev. B* **64**, 04510 (2001).
- [2] G.P. Holland, D.A. Buttry, and J.L. Yarger, " ^7Li NMR Studies of Electrochemically Lithiated V_2O_5 Xerogels." *Chem. Mat.* **14**, 3875 (2002).
- [3] S. Sampath, C.J. Benmore, K.M. Lantzky, J. Neuefeind, K. Leinenweber, D.L. Price, and J.L. Yarger, "Structure of Permanently Densified GeO_2 glass", *Phys. Rev. Lett.* **90**, 115502 (2003).
- [4] S. Sampath, K.M. Lantzky, C.J. Benmore, J. Neuefeind, J. Siewenie, P. Egelstaff, and J.L. Yarger, "Structural Quantum Isotope Effects in Amorphous Beryllium Hydride", *J. Chem. Phys.* **119**, 12499 (2003).
- [5] C.J. Benmore, J. Weber, S. Sampath, J. Siewenie, J. Urquidi, and J.A. Tangeman, "A Neutron and X-ray Diffraction Study of Calcium Aluminate Glasses", *J. Physics: Condensed Matter* **15**, S2413 (2003).
- [6] M.C. Wilding, C.J. Benmore, J. Tangeman, and S. Sampath, "Coordination Changes in Magnesium Silicate Glasses", *Europhys. Lett.* in press (2004).
- [7] S. Sampath, C.J. Benmore, K.M. Lantzky, J. Neuefeind, K. Leinenweber, D.L. Price, and J.L. Yarger, Research Highlights for the Advanced Photon Source Research Activities Report, in press (2004).
- [8] M. Guthrie, C. Tulk, C. Benmore, J. Xu, J.L. Yarger, H. Mao, and R.J. Hemley, "The Formation and Structure of a Dense Octahedral Glass", submitted to *Nature* (2004).