ROLE OF STRUCTURE IN ION MOVEMENT OF GLASSES

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1. Introduction:

The ion movement in inorganic glasses is key to their optimum use in various applications such as solid electrolytes, durable nuclear waste form, stable insulation in electronic devices etc. It is well known that the most common species responsible for the transport properties of inorganic glasses are the mobile monovalent cations, M^+ (or anions). They are predominantly responsible for the dynamic response of glasses under the application of an electric field below the glass transition temperature (T_g). Glass network forming cations (NFCs) have negligible diffusivity and, therefore, do not contribute to the dynamic response directly. Nevertheless, the NFCs, along with oxygen atoms (in oxides), form glass network and provide the framework through which an M^+ can move, thus indirectly determining the ultimate dynamic response of the glass. Then, it appears logical that the local structure of glass (including both the network and the local environment of mobile ions) should play an important role in determining the ionic conduction. However, a correlation between the structure (disorder, network configuration, coordination, homogeneity around the moving ion etc.) and ion dynamics has not been established. The ion jump mechanisms are at the foundation of the latest theoretical developments of the subject, but little is done in the past many years to establish them clearly. Therefore, the primary objective of this project was to understand ion movement in relation to the physical structure of inorganic glasses.

Five different glass forming systems were selected for systematically varying different aspects of the structure and determining their influence on ion dynamics: (1) binary Rb and K germanate glass series; (2) mixed (Rb, Ag) and (Rb, K) germanate glass series (3) high purity quartz

amorphized by neutron irradiation (4) sodium triborate glasses with different melt conditions and (5) heavy metal fluoride glasses. A two-pronged research program was developed: on the one hand dc ionic conductivity and ac relaxation were measured for a variety of oxide and fluoride glasses as a function of composition, temperature and frequency to characterize long and short range ion transport phenomena. The ion movement was also observed in terms of nuclear spin relaxation rate at University of Dortmund, Germany (in collaboration with Professor O. Kanert). On the other hand, the structure was characterized by high resolution x-ray photoelectron spectroscopy (XPS) at Lehigh, infra-red (IR) and Raman spectroscopy at National Hellenic Research Foundation, Athens, Greece (in collaboration with Dr. E. I. Kamitsos), and extended x-ray absorption fine structure (EXAFS) experiments at National Synchrotron Light Source, Brookhaven National Laboratory (in collaboration with Dr. M.A. Marcus of AT & T Labs and Dr. G. Meitzner of Exxon). The most significant results of the project are briefly summarized in the next section. The details of the work are described in 25 publications (see Section 2.1) . The results have been also presented at approximately 45 seminars, national and international meetings, symposia etc.

2. Summary of the Most Significant Observations and Conclusions

(a) The Spatial Homogeneity of Glass Structure: The variation of molar volume with composition of alkali germanate glasses does not correlate with that of various interatomic distances. This has led us to postulate spatial inhomogeneity in glass structure, which is macroscopically represented by the 'unoccupied volume'. It suggests that there exists a non-

uniform spatial distribution of ions, which is relatively independent of the short range structure.

The unoccupied volume provides pathways for the easy diffusion of atoms.

(b) **The Chemical Homogeneity of Glass:** Currently there is considerable discussion about the chemical distribution of alkali atoms such as in the form of clustering or channel formations in the structure. In particular, a modified random network (MRN) model is postulated to replace Zachariasen's classical random network model. Our ambient and low temperature EXAFS results show that the structural disorder around alkali ions in germanate glasses is relatively larger than that around alkali ions in silicates, suggesting that, if at all, the MRN model is less appropriate for the germanate than for the silicate glasses. In other words, we should not rush to discard the random network model. In stead, we should allow for varying degree of non-randomness depending on the glass system.

(c) **The Origin of Germanate Anomaly in Ion Transport:** With the addition of alkali oxide, the properties of germanate glasses show anomalous behavior compared to analogous silicates. This 'germanate anomaly' has been explained in the literature by a $\text{GeO}_4 \rightarrow \text{GeO}_6$ conversion with each molecule of alkali oxide added. However, we find that in addition to this conversion, non-bridging oxygens (NBOs) are also formed for all compositions. A combination of GeO_6 and NBO formation is needed to accurately describe the composition dependence of the properties.

Unlike for the binary alkali silicate glasses where the activation energy for dc conductivity decreases monotonically with alkali concentration, the activation energy for the binary alkali germanate glasses shows complex variation with a small maximum at ~ 10 mol% alkali oxide concentration. This complex variation of activation energy offers a test for the applicability of the

various models of dc conductivity. Thus, the "cooperative ion movement" model recently proposed for silicate glasses is found to be inappropriate for describing ion conduction in germanates, presumably because the strain energy, which is important in germanate glasses, is excluded in the current version of this model.

(d) **On the Origin of the Mixed Mobile (Alkali) Ion Effect:** The mixed mobile (alkali) ion effect is one of the most intriguing phenomenon of glass science. From time to time suggestions are made in the literature that there is a structural origin of this phenomenon. To establish this fact we have determined the structure of two mixed mobile ion glass series. For the (Rb, Ag) mixed mobile ion germanate glasses, the presence of Ag seems to have little effect on the local structure around Rb and Ge atoms. Replacement of Rb by Ag in mixed mobile ion glasses has the same effect on the Rb-O distance and the disorder around Rb as the reduction of the Rb content in binary Rb germanate glasses, probably due to the high deformability of Ag atoms. For the (Rb, K) mixed mobile ion germanate glasses, replacement of Rb by K does not seem to affect the respective local environments around the Rb, K and Ge atoms. In both series, the monotonic change in molar volume or excess volume with composition does not correlate with that of various interatomic distances. The various interatomic distances and structural disorder, which show little variation, do not seem to be the key for the development of MMI effect. In short, the effect is more likely to arise from the dynamics of atoms rather than from the details of static glass structure.

(e) **Can the Melt Structure Affect Glass Properties?:** According to the conventional wisdom, the structure of glass is set around T_g . It does not retain any memory of the liquid state much above T_g . However, using a specially designed experimental procedure we have established that the melt

conditions are observed to affect the structure and properties of sodium triborate glass. This must be due to some extremely slow relaxations in the glass structure. Furthermore, we find an anomalous expansion of the glass melt at 850 °C (similar to that of water below 4 °C), which occurs slowly after it is cooled from 1400 °C. The origin of the anomalous expansion is in the transformation of tetrahedrally coordinated boron to less compact triangularly coordinated boron structural units.

(f) **On the Origin of Electrical Relaxation in Glasses:** The behavior of time or frequency dependent ionic conductivity has been believed to arise from interactions among the mobile ions. The nature of these interactions has been largely unknown or controversial. The previous attempts are shown to have limited validity for correlating conductivity relaxation with the magnitude of dc resistivity, the decoupling index, the activation energy of conductivity or average ion-ion distance. In the past the actual structure of the ionic conductor was never taken into account. The present experiments on quartz crystal, as a model for low ion concentration solid, illustrate that: the conductivity relaxation is determined by the distribution of mobile ions, and the interaction between the mobile cation and its charge compensating centers rather than just among the mobile cations. An anomalous variation of conductivity relaxation is observed with dc conductivity activation energy. A model, which recognizes a common basis for non-randomness in ion jumps and conductivity relaxation, is proposed for explaining all the observations for this system.

(g) **Breakdown of Correspondence between Electrical and Nuclear Spin Relaxation:** Both the electrical relaxation (ER) and nuclear spin relaxation of (NSR) are determined by ion movement in glass. However, it was not known whether or not the two techniques perceive ion movement in the

same way. This has been a puzzle in the field for several years until a correspondence between ER and NSR was established for oxide glasses as expected from the 'fluctuation-dissipation theorem' of statistical thermodynamics. Subsequently, our results on fluoride glasses, unlike those on numerous oxide glasses, reported the first example in which a simple correspondence between NSR and ER breaks down. To explain this discrepancy we note that both ECR and NSR arise from ion-ion interactions. However, in an NSR experiments the ion movement relaxes nuclear spins via dipolar interactions which vary as r_{ij}^{-3} where r_{ij} is the distance between i^{th} and j^{th} moving ions. In contrast, electrical transport, which relates to diffusion via Nernst-Einstein relation, depends on mean square displacement. Thus the ion-ion interactions affect the correlation functions for NSR and ER differently. The important message is: even if the primitive ion jump is the same, the perception of ion-ion interactions, which determines our observations, is sensitive to the technique employed.

3. List of Publications

(* $\Rightarrow$ An invited contribution)

- *1. Ion Movement Relaxation in Inorganic Glasses - Salient Features.
H. Jain, J. Non-cryst. Solids, 131, 961 (1991).
(Received the best paper presentation award at International Meeting on Relaxation in Complex Systems, Crete, Greece, 1990.)
- *2. X-ray Photoelectron Spectroscopy for Understanding Ionic Conduction in Glasses.
H. Jain, C.H. Hsieh and O. Kanert, Trans. Ind. Ceram. Soc. 50, 14 (1991).
3. Study of Dynamic Properties of Fluoride Glasses by Nuclear Magnetic Resonance
S. Estalji, O. Kanert, J. Steinert, G. Balzer-Jollenbeck, H. Jain and K. L. Ngai
Mater. Sci. Forum, 67 & 68, 607 (1991)
4. Nuclear Spin Relaxation in Fluorozirconate Glass
O. Kanert, R. Kuchler, S. Estalji, K.L. Ngai and H. Jain, The Physics of Non-crystalline Solids,
L.D. Pye et al. eds., Taylor and Francis, 1992. p. 178.

5. On the Nature of Bulk Electrical Relaxation in Silicate Glasses
W.K. Lee, S. Aronson-Unger, J.F. Liu, A.S. Nowick and H. Jain, L.D. Pye et al. eds., Taylor and Francis, 1992. p.332
6. Nuclear Magnetic Resonance and Ionic Motion in Fluorozirconate Glasses.
S. Estalji, R. Kuchler, O. Kanert, R. Bolter, H. Jain and K.L. Ngai, J. Physique, Pt IV, vol. 2, 159 (1992).
- *7. Ionic Motion in Inorganic Glasses
H. Jain and O. Kanert
Defects in Insulating Materials, O. Kanert and J.-M. Spaeth, eds., World Scientific, 274 (1993).
8. Study of Ionic Motion in Fluorozirconate Glasses by NSR and Electrical Conductivity
S. Estalji, R. Kuchler, O. Kanert, R. Bolter, H. Jain, and K. L. Ngai
Defects in Insulating Materials, O. Kanert and J.-M. Spaeth, eds., World Scientific, 973 (1993).
9. An Explanation of Significant Differences between Nuclear Spin Relaxation and Conductivity Relaxation
R. Kuchler, R. Bolter, O. Kanert, H. Jain and K.L. Ngai
Defects in Insulating Materials, O. Kanert and J.-M. Spaeth, eds., World Scientific, 1321 (1993).
- *10. Measurement of Electrical Conductivity of Glasses
H. Jain
Experimental Techniques of Glass Science, C.J. Simmons and O.H. El-Bayoumi, eds., American Ceramic Society, 433 (1993).
11. Anomalous Expansion of Sodium Triborate Melt and Its Effect on Glass Properties
W. C. Huang, H. Jain, E. I. Kamitsos and A. P. Patsis
J. Non-cryst. Solids, 162, 107 (1993).
12. Significant Differences between Nuclear Spin Relaxation and Conductivity Relaxation in Inorganic Glasses
O. Kanert, R. Kuchler, K.L. Ngai and H. Jain
Phys. Rev. B49, 76 (1994).
13. Study of nuclear spin relaxation in CLAP glasses
R. Kuchler, M. Fricke, O. Kanert, H. Jain and K.L. Ngai

- J. Non-cryst. Solids 172, 1373 (1994)
- *14. Importance of structure in electrical conductivity relaxation
H. Jain and W.C. Huang
J. Non-cryst. Solids 172, 1334 (1994)
15. Structural study of Rb and (Rb, Ag) germanate glasses by EXAFS and XPS
W.C. Huang, H. Jain and M.A. Marcus
J. Non-cryst Solids 180, 40 (1994)
16. Correlation between local structure and electrical response of Rb and (Rb, Ag) germanate glasses: dc conductivity
W.C. Huang and H. Jain
J. Non-cryst Solids, 188, 254 (1995)
17. Variation of atomic scale density in oxide glasses
H. Jain and W.C. Huang
Proc. ACerS Glass & Optical Materials Division 1994 Fall Meeting. M. K. Choudhary and D. M. Krol, eds. American Ceramic Society, Westerville, OH. p 25 (1994)
18. Significance of the disorder induced by neutron irradiation for electrical relaxation in SiO_2
H. Jain and W.C. Huang
J. Non-cryst. Solids, 196, 267 (1996)
19. The structure of potassium germanate glasses by EXAFS
W.C. Huang and H. Jain
J. Non-cryst. Solids, 196, 155 (1996)
20. Structure of Potassium and Rubidium Germanate Glasses by X-ray Photoelectron Spectroscopy
X. Lu, H. Jain and W.C. Huang
Phys. Chem. Glasses, accepted for publication, in press (1996)
21. A Comprehensive View of the Local Structure Around Rb in Rubidium Germanate Glasses
H. Jain, E.I. Kamitsos, Y. Yiannopoulos, G.D. Chryssikos, W.C. Huang, R. Kchler, and O. Kanert,
J. Non-cryst Solids, accepted for publication, in press (1996)
22. Correlation Between Far Infrared Absorption and Electrical Conductivity of Rubidium Germanate Glasses
E. I. Kamitsos, Y. Yiannopoulos, H. Jain and W. C. Huang

- J. Non-cryst Solids, accepted for publication, in press (1996)
23. Raman and Infrared Structural Investigation of $x\text{Rb}_2\text{O} - (1-x)\text{GeO}_2$ Glasses
E. I. Kamitsos, Y. Yiannopoulos, M.A. Karakassides, G.D. Chryssikos and H. Jain
J. Phys. Chem., accepted for publication, in press (1996).
 24. Far Infrared Spectra of Alkali Germanate Glasses and Correlation with Electrical Conductivity
E. I. Kamitsos, Y. Yiannopoulos, H. Jain and W. C. Huang
Phys. Rev. B., accepted for publication, in press (1996).
 25. Electrical conduction in relation to local and intermediate range structure of rubidium germanate glasses
H. Jain, W. C. Huang, and E.I. Kamitsos
Proc. MRS Symp. Electrically Based Microstructural Characterization, in press (1996).

4. Suggestions for Future Work

In recent years one of the most vigorously debated topic concerning the glass structure is the chemical distribution and homogeneity of the various species. The previous EXAFS work led to the modified random network model for the lack of chemical randomness. By contrast, the present EXAFS work has shown that the chemical homogeneity can vary significantly from one glass system to another. To resolve this issue we need a direct chemical map of the glass structure, which is obtained by using state-of-the-art electron microscopy techniques such as EXELFS.

As the homogeneity and randomness of glass structure is established, in parallel one needs to establish what effect they could/would have on various glass properties. For example, the present results show that the phenomena like the mixed alkali effect exist independent of the extent of chemical randomness. Some properties are more dependent on the dynamics than on static structure. These correlations need to be established by measuring other properties (mechanical, chemical, transport,

optical etc.) on glass systems with significantly different structures. In addition, the role of spatial homogeneity needs to be assessed. This aspect of glass structure has been generally ignored in the past - except that we have seen it to be the most important factor in relation to long range diffusion in germanate glasses.

The experiments on sodium borate melt have shown sufficiently convincingly that it is possible for a glass to remember the melt state from which it was quenched. Further evidence is emerging in the literature in support of this revolutionary concept. These observations have challenged our fundamental understanding of glass formation and structural relaxations. Further work must be undertaken first to verify our observations and then to develop a comprehensive understanding of glass formation.

Ion dynamics is shown to be a complex phenomenon consisting of several mechanisms which dominate in different regions of time (frequency) and temperature. In the past one learnt about different mechanisms by changing frequency of electrical signal and sample temperature. However, the future progress will come by combining with the variation of temperature, frequency and temperature, a variety of techniques which perceive ion movement with different emphasis.