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"THE ROLE OF MOBILE ION'S IN FAST ION CONDUCTING SYSTEMS, AND
HIGH IMPACT STRENGTH CERAMICS"
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BY

C.A. ANGELL
DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY

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"THE ROLE OF MOBILE ION'S IN FAST ION CONDUCTING SYSTEMS, AND HIGH IMPACT STRENGTH CERAMICS"

INTRODUCTION

This report summarizes the proposed ideas and accomplishments of work performed under DOE support since the grant support was initiated in 1984. For the most part the text follows the "accomplished work" section of the new proposal prepared for DOE when the primary investigator moved his laboratory from Purdue University to Arizona State University in 1989. This text is modified where necessary in the light of later developments and updated with respect to published works. Items then referred to as papers in preparation which are now published, are attached as Appendices. Those items referred to as Appendices for which full reports were previously submitted to DOE with the proposal, will be represented here by their abstract pages.

The period of research summarized in this final report has been a productive and satisfying one and many of the accomplishments reported have already received a pleasing degree of recognition by the scientific community in the form of plenary and invited speaker invitations etc. These are listed in a separate section of the report following the listing of published works.

Our original proposal sought to establish conditions under which two new types of materials might be developed. (1) A glassy material in which the current is conducted by mobile divalent cations, (2) a polymeric material in which the chain which provides elastomeric properties itself possesses repeating ionic charges and a counter ion so that it

could serve as one component in a salt solution which would be conducting because the second component would contain a cation of high mobility, Ag^+ or Li^+ . We describe in the following sections the failure of these ideas and the success of the ideas which these failures provoked.

RESEARCH OBJECTIVES AND ACCOMPLISHMENTS

1. Polymeric Systems

In a preliminary research period of one year prior to the reconstitution of the contract into its current grant form, we had already shown that the second of these objectives can probably not be met for the reason outlined in the 2nd paragraph, of the previous section. Therefore while the notion was retained in the title of the present grant for the sake of continuity, the aim was substituted with a proposal to exploit an idea which the early work had spawned, namely the use of organic cations to prepare a solid solution or an ionic crystal phase with free rotation characteristics, i.e. plastic crystal phases in which cations could be aided in their motion by the freely rotating anionic constituents.

During the present grant period I.M. Cooper succeeded in synthesizing several compounds which expressed the latter idea, and showed that some of them had highly interesting conductivity characteristics. This work is fully documented in a paper presented at the 1985 International Conference on Solid State Ionics which was submitted to DOE earlier.

Since Cooper's departure in early 1985, this work has lain undeveloped until very recently when a new student, Don List, joined the program. List has now tested the performance of

another of Cooper's compounds which had a phase transition which lead to its identity, in the Cooper paper, as a promising prospect for future work.

Evidently the new compound is indeed superior and we hope to develop it into a very competitive material for solid state devices, rivalling some of the more recently developed polymer-salt systems.

2. Lead halide-containing fast ion conducting glasses.

In an initial endeavor to develop glasses in which divalent cations might be mobile, lead halides were doped into lead metaphosphate and a wide range of glass forming compositions was revealed. The conductivity of the high halide containing glasses was quite impressive, and the question of which ion was the mobile species could not be clearly answered. The activation energy for the bromide-doped glasses was lower than for the chloride-doped glasses which is what would be expected for a mobile lead species. On the other hand, the chloride-doped glass was the better conductor due to higher pre-exponential factor, and with the recent development of closely-related highly-conducting fluoride-doped glasses, described in the next paragraph. The balance of evidence indicates that the conducting species is in fact the halide ion. Thus the high mobility of Pb^{2+} found in the β -alumina structure PbF_2 is not reproduced in these glassy systems. Assuming the conducting species was indeed the anion, these glasses at the time of development represented the best anion conducting vitreous materials yet reported. A description of the work is contained in Appendix I, ^{*} which was also presented at the fifth International Meeting on Solid State Ionics in 1985.

** paper No. 4*

If indeed the conductivity is anionic then it would be expected that the lead fluoride doped glasses would be far better conductors still since PbF_2 is an excellent crystalline solid fluoride ion conductor. In the PbF_2 - $\text{Pb}(\text{PO}_3)_2$ system, however, the glass-forming range is very limited and the glasses are very poor conductors. In a follow-up of this work A.R. Kulkarni in this lab has found that with the replacement of the $\text{Pb}(\text{PO}_3)_2$ with $\text{Al}(\text{PO}_3)_3$ in the binary system containing lead fluoride, glasses can be obtained at very high PbF_2 contents. These glasses prove to be excellent conductors, and there can be little doubt that this is due to the high mobility of fluoride ions in the glass matrix. These systems are evidently acquiring something of the characteristics of crystalline PbF_2 . Kulkarni also found that the aluminum metaphosphate could be reduced still further if MnF_2 is added as a third component. In such ternary glasses record breaking (by approximately two orders of magnitude) conductivities have been measured. The results of this work recently appeared in print and an abstract is attached as Appendix II. (paper no. 11)

Since Kulkarni has had previous experience in the high cationic conductivity of the system LiF - $\text{Al}(\text{PO}_3)_3$ the question of behavior on mixing the fast cation and the fast anion systems arose. A series of experiments were therefore carried out on the ternary system LiF - PbF_2 - $\text{Al}(\text{PO}_3)_3$. We found that, reminiscent of the mixed alkali effect in silicate and other oxide glasses, the conductivity in the pseudobinary system containing a fixed proportion of $\text{Al}(\text{PO}_3)_3$ goes through a minimum at some intermediate composition. It would appear from this that the presence of a mobile cationic species inhibits the motion of a mobile anionic species and vice-versa. We observed that the minimum in conductivity corresponds to a maximum in activation energy. On the other hand, caution must be exercised in view of the fact that the glass transition temperature also passes through a minimum in the vicinity of the conductivity minimum. This raises the possibility that the

conductivity minimum is to be associated with the lower fictive temperature ($T_F \propto T_g$ for fixed thermal history) for the low-conducting glasses. In other words, the minimum in σ would be reduced, and might even disappear, if the glasses of high glass transition temperature were to be annealed so that their structures equilibrated at temperatures of the same value as the glass transition temperature at the composition of the conductivity minimum. Alternatively, this problem can be posed by asking the question "Would there be a conductivity minimum if all measurements were carried out in the *liquid* state rather than on examining the behavior after equilibrium has been lost at the glass transition temperature?"

While we cannot respond with confidence to the latter question without performing many additional measurements, we *can* state with confidence that the decoupling index, R_τ [defined as the ratio of the structural relaxation time for the matrix to the conductivity relaxation time (determined by the mobile subset of ions)] passes through a minimum at a composition close to that of the isothermal conductivity minimum. This is because the structural relaxation time at T_g is always about 200 seconds, and the electrical relaxation time is dominated by the value of the d.c. conductivity. Their ratio R_τ passes through a minimum.

With the mixed alkali effect in mind, we have performed some measurements of mechanical relaxation via mobile ions on this mixed cation-anion conducting system. In the case of the mixed alkali effect it is found that there is a major enhancement of the mechanical loss (dissipation of a mechanical energy from an oscillating stress field) caused by the presence of two dissimilar cations. It was thought that, to the extent that the present phenomenon might be related to the mixed alkali effect, a maximum mechanical loss might be found in

the vicinity of the conductivity minimum in the present case. We found no maximum in the mechanical loss, $\tan \delta$, corresponding with mixing of mobile cations and anions, and the only effect of note is an apparent broadening of the loss curve. When the data are plotted vs. reciprocal temperature (which is the appropriate plot when the half widths of loss peaks with maxima at different temperatures are being analyzed) we observe a weak maximum at 60% LiF. However, the losses are all small, and since we could not make samples over the whole range, we can only conclude that no strict analog of the mixed alkali effect exists.

In future work further elucidation of these phenomena will be sought via transport number measurements for cations and anions, and possibly electrochemically determined diffusion coefficients, e.g. of Ag^+ ion doped into the glass, determined in the vicinity of the conductivity minimum. It is expected that the silver ion diffusivity (reflecting the lithium of ion conductivity) will decrease monotonously through the conductivity minimum.

Some of these accomplishments have been described in a multi-author paper dealing with studies of fast cation and fast anion motion in glassy substances which was presented at the International Congress on Glass held in New Delhi in 1988 (see Appendix III a and b).

(See papers 7 and 8)

3. Mixed ionic electronic conduction.

Since successful electrochemical devices based on solid state materials require at some point that electrons be conducted within a medium contacting the purely ionic conductor, we decided to investigate materials which conduct, under the right circumstances, via both electrons and ions. The project was based on the idea of combining electrical and mechanical measurements to provide a means of separating the situation in which ions

alone can conduct. The idea, in essence, is that when ions jump, a substantial volume change can occur and that this is reflected quite strongly in the response to a mechanical stress, and the mechanical energy loss occurs due to the jumping of ions. However, when an electron jumps, very little volume change occurs, a much smaller mechanical response might be anticipated. Thus a combination of mechanical and electrical measurements should be able to distinguish between the electronically conducting and ionically conducting regimes. These measurements were carried out by Prof. K.H. Kim during a sabbatical leave in this laboratory, and the results may be summarized as follows (some inconsistencies in the data have however, been noted in writing up this work and nothing is being published until the origin of these inconsistencies has been clarified).

When Na_2O is added to the electronically conducting mixed oxide $\text{V}_2\text{O}_5\text{-TeO}_2$, the following phenomena are observed:

- (i) the total conductivity increases rapidly and by the glass-forming limit at fifty mole percent Na_2O , it has reached a value which is equal of the best sodium ion conducting glass yet reported (the $\text{Na}_2\text{S-GeS}_2$ glass reported by Susman et al.).
- (ii) the mechanical loss observed at 110 Hz during temperature scans, which is negligible in the absence of Na_2O additions, increases systematically with Na_2O content. Simultaneously, the temperature at which the peak loss is observed moves to lower values as expected when the conductivity by ions increases.
- (iii) the temperature dependence of conductivity follows an Arrhenius Law at high temperatures in the presence of sodium oxide but returns to curvilinear behavior typical of a small polaron hopping conductance mechanism at low temperatures in all cases.
- (iv) the temperature at which the conductivity relaxation time calculated from the high temperature Arrhenius part of the conductivity plots reaches $(110 \text{ Hz})^{-1/2\pi}$ the

cycle time of the mechanical relaxation experiment, corresponds well with the temperatures at which the mechanical loss at 110 Hz reaches a maximum. This is evidence that the high temperature plots of the conductivity parts are dominated by ionic conductivity, while conversely, the low temperature parts are due to electronic conductivity.

4. Plastic crystals.

Don List has now made an extensive study of binary plastic crystal systems consisting of succinonitrile, $\text{CN-CH}_2\text{-CH}_2\text{-CN}$ with second components containing one more or one less carbon atom in the chain. The binary systems show extensive regions in which the plastic crystal transition of succinonitrile is suppressed with the result that the plastic crystal state can be converted continuously into a "glassy crystal" state. The glass transition temperatures in each case are found to be very weak functions of composition. This means that in several systems the properties of the plastic state during continuous slow-down can be monitored without fear of crystallization, and a great deal about the physics of plastic crystals can be worked out.

Preliminary studies on the solubility of ionic substances in these plastic crystals phases has given ambiguous results. Systems which appear to be homogeneous solid solutions, which indeed have very high conductivities, have been prepared but the predicted thermodynamic effects of the plastic crystal transition in the succinonitrile-rich systems have not been in accord with expectations. This means that the establishment of true solid solutions containing disassociated ions has not yet been proven. It is possible that the

conductivity effects we see are due to grain boundary liquid phases. We hope to clarify this matter in the coming research period.

5. Mobile ions as a basis for high impact ceramics.

This project is a way to a good start, with an apparent verification of the original premise and some rather striking comparisons between the proposed high impact glasses and conventional glasses such as pyrex, as the main achievements.

The intention was to demonstrate that glasses in which a subset of the ions could move rapidly in response to a stress would have a much greater resistance to failure under impact than ordinary glasses. Our initial tests have been based on comparison of the behavior of rods of pyrex glass, which has no electrical conductivity, with rods of the same dimension of glasses characterized in our previous DOE-supported work as being fast ion conductors. To make these tests we purchased a Kravitz Impact Tester and modified it so that we could distinguish the effects of total energy necessary to cause failure from the impact necessary to initiate the failure. The modification will be described in a future report. For the moment we note that where there was little difference between the fast ion glasses and the total energy necessary to cause failure, very striking increases in resistance to the impact that the glass would withstand *without* failure were recorded for glasses with high conductivity. The test cases were borates of the alkali metals Li, Na, K, and Cs. Of these the former two were known as rather good fast ion conductors. Rods of the potassium and cesium borates failed at an impact parameter of ~6 on our arbitrary scale, essentially the same as for pyrex rods. Rods of the lithium and sodium borates, by contrast, failed at impact parameters which reached as high as 19 on the same arbitrary scale. In all cases

there is a wide range of impact parameters at failure, which was expected in view of the sensitivity of glass to the precise nature of the surface.

Attempts to reduce this effect by improving techniques for the production of rods, or by various surface etching or protection treatments, have so far failed to significantly reduce the scatter of the measurements.

At this early stage we feel very encouraged by these results and will consider shortly filing a patent application based on the type of data which we are reporting above.

6. Other Accomplishments.

Besides the above work which has followed the principal lines anticipated in the original proposal, three small projects, which extend our capabilities in the field of glass science and fast ion conductors, have been included in the course of ongoing work. One of these has been reported already (in the proceedings of the recent International Congress on Glass), a report on the second is in the galley proof stage, and a manuscript on the third is about to be submitted. We describe these, and their relation to the main line of work, in the following paragraphs.

(i) The α relaxation in ionic glasses.

All the fast ion glasses in the work described above depend for their character on the decoupling of the modes of motion of one subset of the systems particles from the

remainder (matrix). The motions of the matrix are frozen out at the glass transition, and it is important to understand something of the mechanics of this process if we are to fully understand the kinetics of the fast ion relaxation. Therefore a set of experiments utilizing, in a new manner, the same instrument used in mechanical relaxation studies of the fast ion motion, were carried out. We studied the classical glass-forming molten salt system $\text{Ca}(\text{NO}_3)_2\text{-KNO}_3$; rods of the glass were prepared from the anhydrous melt of composition 40 mol% KNO_3 and were mounted in a stirrup of quartz glass in the flexural mode for analysis by stress relaxation using the Rheovibron. This work is fully described in Appendix IV. The essential feature is to instantaneously impose a strain on the flexed sample and then watch the decay of the induced stress as a function of time as the sample slowly distorts by the viscoelastic relaxation process. These measurements allow the determination of the non-exponentiality, as well as the non-linearity, of the glassy relaxation. Relaxation times obtained in this way have been compared with those obtained on shorter time scales using alternative techniques, and extend the range of direct τ data on this system to 14 decades.

(ii) The glass transition in P_2O_5 and viscosity-temperature relations.

A detailed study of fast ion conduction in alkali phosphate glasses was performed by S.W. Martin under the auspices of the Purdue NSF-MRL Program. When that program terminated in 1984, Martin who was approaching the end of his Ph.D. thesis, was taken

onto the DOE grant while he completed his project and wrote his thesis. During this time it became evident that the end member of the glassy series, P_2O_5 itself had been inadequately characterized in the literature. For this reason a short project in which melt-formed P_2O_5 glasses were analyzed using the Perkin-Elmer DSC-2 Differential Scanning Calorimeter was undertaken. This work proved very interesting and formed the basis of a paper that has appeared in *J. Phys. Chem.* The main feature is that P_2O_5 seems to be even more Arrhenius in its transport properties than the classical SiO_2 .

(iii) Conductivity transition between all-halide and all-oxide glasses.

During this grant period, glasses in which the only anion present is a halide have been developed under other auspices (support of ONR). A question of interest arose involving the behavior of the conductivity in these unusually highly conducting glasses as they are blended into a more conventional oxide glass. This question intrigued H.G.K. Sundar who had been working on the DOE grant and he undertook a short series of experiments in which the halide glass $AgI-CsCl$ was mixed continuously with the oxide glass $AgI-Ag_2P_2O_7$. Sundar was able to attain miscibility across 90% of the pseudobinary system, and obtained rather interesting conductivity results. In essence, the linear $\log \sigma$ vs. -mol % halide relation found in earlier studies of classical systems such as $AgPO_3-AgI$ was lost, and instead a strongly curvilinear function was found. A general interpretation was given in terms of a transition between two basically different types of conducting structures, one characteristic of the oxy-halide glasses and the other characteristic of the all-halide glasses. Details are given in Appendix V. (See paper 12)

Invited Lectures and Seminars Based on DOE-supported Research
1984 - 1989
Grant No. DE-FG02-84ER45102

1. "Spectroscopic and Computer Simulation Studies of Ion Dynamics in Liquids and Superionic Glasses," Chemistry Departmental Colloquium, Texas A&M, College Station, Texas, April 12, 1985. (invited).
2. "Fast Ion Phenomenology in Glassy Solids," Transport in Solids Symposium, American Chemical Society National Meeting, Miami, Florida, May 2, 1985. (invited).
3. "Relaxation Near the Glass Transition," Symposium on the Glass Transaction, American Ceramic Society Spring Meeting, Cincinnati, Ohio, April 7, 1985. (invited).
4. "Recent Advances in Glassy Electrolyte Transport," Plenary lecture, 6th International Congress on Solid State Ionics, Lake Tahoe, California, August 21, 1985. (invited).
5. "Long Time Relaxation Processes in Glassy Solids I. α -Relaxations in "Fragile" Systems," H.G.K. Sundar and C.A. Angell, Proc. 14th Congress on Glass, New Dehli, India, March 1-5, 1986.
6. "Long Time Relaxation Processes in Glassy Solids II. β -Relaxations in Fast Ion Conducting Glasses." A. Kulkarni, H. Senapati, Changle Liu and C.A. Angell, Proc. 14th congress on Glass, New Dehli, India, March 1-5, 1986.
7. "Fast Ion Conduction in Glasses," Dept. of material Sciences, Ohio State, May 15, 1986. (invited).
8. "Fast Ion Conduction in Glassy Solids," Inst. of Physics, Chinese Academy of Sciences, May 19, 1986. (invited.)
9. Fast Ion Conduction in glassy Solids," Inst. of Ceramics, Chinese Academy of Sciences, Shanghai, May 28, 1986. (invited).
10. "Fast Ion Conduction in Glassy Solids," Inst. of Chem. Technology and Engineering, Shanghai, May 29, 1986. (invited).
11. "Supercooled Liquids and fast Ion Conducting Glasses," Dept. of Physics, University of Soujou, Soujou, China, May 31, 1986. (invited).
12. "Mechanical V. Electrical Relaxation Processes in Supercooled Liquids and Glasses," Gordon Conference on Dielectric Relaxation, New Hampshire, July 27-31, 1986. (invited).
- 13 & 14. "Overview of Transport Porcesses in Ionic Liquids," and Results and Interpretation of Transport Processes in Molten Salts," Two lectures given to the NATO Advanced Summer Institute on Molten Salts, Camerino, Italy, August 3-17, 1986. (invited).

15. "Relaxation Processes in Liquids + Glasses" presented to the Greater Washinton Solid State Physics Colloquium, Dec. 4, 1986. (invited).
16. "Relaxation in Glassy Systems," presented to participants in the workshop on Relaxation and Kinetics in Complex systems, institute of Theoretical Physics, University of Santa Barbara, Santa Barbara, California, January 12, 1987. (invited opening talk).
17. "Glassy Solid Electrolytes," presented to participants at the workshop on Materials Science, Energy and Development, University of the West Indies, Mona Campus, Jamaica, April 9, 1987. (invited).
18. "Insights Into Ion-Matrix and Ion-Ion Couplings in Polymer-Salt Electrolytes from Relaxation Spectroscopy," presented to participants of the International Symposium on Polymer Electrlites, University of St. Andrews, Scotland, June 17, 1987. (invited lecture).
19. "Decoupling of Univalent Cation Motions from Viscosity in Univalent Ion Salt Mixtures," presented to scientists attending the Fifth International Symposium on Molten Salts at the Fall Meeting of the Electrochemical Society, Honolulu, Hawaii, October 19-23, 1987.
20. "Ionic Mobility in Crystal and Glasses," presented to scientists and students of Laboratoire du Chemie du Solide, University of Bordequx, July 9, 1988.
21. "Vitreous Solids: The New Solid Electrolytes," presented to scientists attending the US-India workshop on Glasses, Bangalore India, Nov. 17-19, 1988.
22. "Glassy Solids and DC Conductivity in the Liquid and Glassy States," presented to scientists at the Materials Science Center, Tata Institute, Bombay, India, Nov. 25, 1988.
23. "Non-random Mixing and Fast Ion Decoupling in Lithium Chloroborate Superionic Glasses: an Ion Dynamics Computer Simulation Study," by R. Syed, J. Kieffer, and C.A. Angell, presented by R. Syed to scientists attending the Fall Meeting of the Materials Research Society, Boston, Nov. 28, 1988.
24. "AC and DC Studies of Non-exponential Relaxation Processes in Superionic Conductors: Correlation of Conductivity and NMR Studies," by C.A. Angell and S.W. Martin, presented by C.A. Angell to scientists attending the Fall Meeting of the Materials Research Society, Boston, Nov. 29, 1988.
25. "Dynamic Processes in Glasses and Plastic Crystals," presented at the symposium on Dynamics of Condensed Phases, ACS Spring Meeting, Dallas, April 9-14, 1989.

Publications Based on DOE-supported Research
1984-1989
Grant No. DE-FG02-84ER45102

1. "Fast Ion Conductors in Viscous liquids and Glasses," C.A. Angell, in Relaxations in Complex System, ed. K. Ngai and G.B. Wright, National Technical Information Service, U.s. Department of Commerce, Springfield, VA 22161 (1985).
2. "d.c. and a.c. Conductivity in Wide Composition Range $\text{Li}_2\text{O-P}_2\text{O}_5$ Glasses," S.W. Martin and C.A. Angell, *J. Non-Cryst. Sol.* **83**, 185 (1986).
3. "Ambient Temperature Plastic Crystal Fast Ion Conductors (PLICFICS)," E.I. Cooper and C.A. Angell, *Solid State Ionics* **18&19**, 570 (1986).
4. "Glass Formation and High Conductivity in Lead Halide-Lead Metaphosphate Glasses," H.G.K. Sundar, S.W. Martin, and C.A. Angell, *Solid State Ionics*, **18&19**, 437 (1986).
5. "All Halide Superionic Glasses," Changle Liu, H.G.K. Sundar and C.A. Angell, *Sol. State Ionics* **18&19**, 442 (1986).
6. "Recent Developments in Fast Ion Transport in Glassy and Amorphous Materials," C.A. Angell, *Solid State Ionics* **18&19**, 72 (1986) (text of plenary lecture).
7. "Long Time Relaxation Processes in Glassy Solids I," α -Relaxations in Congress on Glass, Collected Papers Indian Ceramic Society Pub. **II**, 161 (1986).
8. "Long Time Relaxation Processes in Glassy Solids II. β -Relaxations in Fast Ion Conducting Glasses," A. Kulkarni, H. Senapati, Changle Liu and C.A. Angell, XIVth international Congresss on Glass, Collected Papers, Indian Ceramic Societty Pub. **II**, 169 (1986).
9. "Glassy Solids and dc Conductivity in the Liquid and Glassy States," C.A. Angell in *Materials for Solid State Batteries*, ed. by B.V.R. Chowdari and S. Radhakrishna, p. 31-40, (1986).
10. "Relaxation Processes in Glassy Solids," C.A. Angell, H.G.K. Sundar, A.R. Kulkarni, H. Senapati and S.W. Martin, in "Molecular Dynamics and Relaxation Phenomena in Glasses," Ed. Th. Dorfmueller and G. Williams, *Lecture Notes in Physics*, Springer-Verlag, **277**, 75-89, (1987).
11. "High Fluoride Ion Conduction and Conductivity Maxima with the Glassy System $\text{PbF}_2\text{-MnF}_2\text{-Pb(PO}_3)_2$," A.R. Kulkarni, H.G.K. sundar, and C.A. Angell, *Solid State Ionics* **24**, 253-257 (1987).
12. "Ionic Conductivity in Wide-Range Halide-Pyrophosphate Glasses," H.G.K. Sundar, Changle Liu, and C.A. Angell, *Mat. Res. Bull.* **22**, 1533 (1987).
13. "Mobile Ion Crossover Effects in the System $\text{LiF-PbF}_2\text{-Al(PO}_3)_3$ From Electrical, Mechanical, and Tg Studies," A.R. Kulkarni and C.A. Angell, *J. Non-Cryst. Sol.* **99**, 195 (1988).

14. "Correlation of Mechanical and Electrical Relaxation Phenomena in Superionic Glasses," C.A. Angell, *Mat. Chem. Phys.* **23**, 143 (1989).
15. "Phenomenology of Fast Ion Conducting Glasses: Facts and Confusions," *Solid Electrolytes*, Ed. T. Takahashi, World Scientific Press, Singapore, 1989, p. 89.
16. "Glass Formation and Conductivity in the Ag₂S-AgPO₃ System: Evidence Against Cluster Pathway Mechanisms for High Ionic Conductivity," L. Jun, J. Portier, B. Tanguy, J-J. Videau and C.A. Angell, *Solid State Ionics* **345**, 87 (1989).
17. "Transition Range Viscosity of Rapidly Quenched Bi-Ca-Sr-Cu-O Glasses," M. Tatsumisago, C.A. Angell, S. Tsuboi, Y. Akamatsu, N. Tohge, and T. Minami, *Applied Phys. Lett.* **54**, 2268 (1989).
18. "Crystallization Kinetics for Quenched Bi-Ca-Sr-Cu-O Glasses," M. Tatsumisago, C.A. Angell, Y. Akamatsu, S. Tsuboi, N. Tohge, and t. Minami, *Appl. Phys. Lett.* **55**, 600 (1989).
19. "Non-Random Mixing and Fast Ion Decoupling Lithium in Lithium chloroborate Superionic Glasses: An Ion Dynamics Computer Simulation Study," R. Syed, J. Kieffer and C.A. Angell, *Symp. Mat. Res. Soc.* **135**, 73 (1989).
20. "Fast Ion Conduction in Glass: the New Solid Electrolytes," C.A. Angell, *Proc. Workshop on Application of Glasses*, Bangalore, India, Nov. 1988. Eds. K.J. Rao, A.R. Cooper and H. Jain, World Scientific Pub., Singapore, 1989, p. 245.

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