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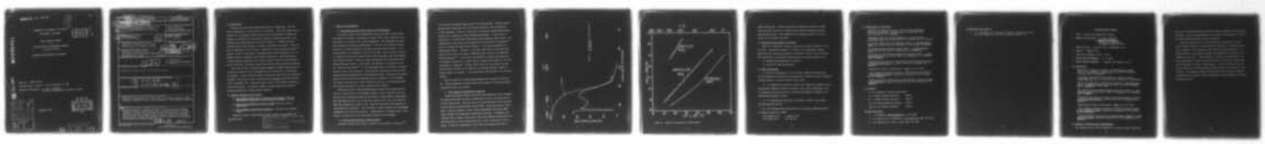

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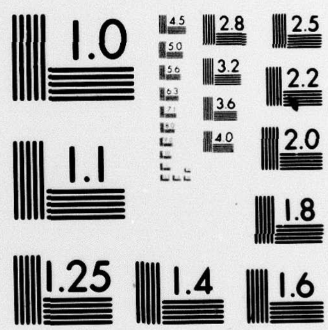
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UNIVERSITY OF CALIFORNIA, LOS ANGELES

LOS ANGELES, CALIFORNIA

FINAL SCIENTIFIC REPORT

to

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

on project entitled

"STRUCTURE AND PROPERTIES OF GLASSES"

Grant No.: AFOSR 79-0019

Inclusive Dates: October 1, 1978 to September 30, 1979

Principal Investigator: Dr. John D. Mackenzie
Professor of Engineering and Applied Science

November, 1979

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7. AUTHOR(s): John D. Mackenzie	8. CONTRACT OR GRANT NUMBER(s): AFOSR-79-0019
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The elastic modulus of glasses are shown to be affected by ion-exchange because of the loss of unoccupied space in the glass network. The water content of beryllium fluoride glasses affects the ionic content although the fluorine ion is the current carrier because of defects in the glass caused by water. Transparent composites have been prepared by impregnating porous glass with polymethylmethacrylate.

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1. Introduction

Glass is one of the most important materials of engineering. The most obvious application for the Air Force is in windows. Other less obvious applications are, for instance, glass fibers for the reinforcement of rubber and plastics, glass fibers for wave-guides, infra-red transmitting lenses, laser components and high reliability electrical connectors. Through controlled crystallization, glass-ceramics of superior properties are prepared. These are also of importance to the Air Force. Because of the non-crystalline nature of glasses, it has not been easy to understand many of their properties nor is it simple to predict properties from chemical composition. The broad objective of this research program was thus to gain a better scientific understanding of how the structure of inorganic glasses could affect various selected properties.

From 1974 to 1978, a research program supported by AFOSR through Grant No. 75-2764 was carried out in our laboratories at the University of California, Los Angeles. A Final Scientific Report covering that period has been separately prepared. This report is only concerned with the one-year period from October 1978 to September 1979. During this period, some of the research initiated in 1977 were continued. In addition research on oxide glasses was extended to fluoride glasses and to glass-polymer composites.

2. Research Conducted in this Period

a) Relationship between Elastic Modulus and Ion-exchange. This was essentially a continuation of the research initiated in 1977-78.

b) Structure and Properties of Halide Glasses. This was a new research topic.

c) New Transparent Glass-Polymer Composites. This was a new research topic.

Important research accomplishments within the above three projects are described below.

3. Research Accomplishments

a) Relationship between Elastic Modulus and Ion-Exchange.

If a glass is kept at some temperature below T_g and small cations within its network are allowed to exchange with larger cations from a fused salt bath, the surface of the glass will be under compression. This phenomenon has been widely exploited for glass strenghtening.[1] How this "ion stuffing" process can affect the elastic modulus of the glass has never been discussed. In our current project, we considered it for the first time. When a stress is applied to a glass, the strain can take the form of bond stretching, bond angle bending and rotational motion of ions (e.g. SiO_4 tetrahedrons) into "unoccupied space" within the glassy network. Silica glass, for instance, is calculated to have 30 - 40% unoccupied space.[2] If this unoccupied space is decreased, rotational motion of ions is more difficult. Strain now must take place via bond stretching and bond angle bending which involve greater energy. Effectively the elastic modulus should increase when unoccupied space is decreased. In ion-exchange, big cations take the place of small cations at below T_g. Thus unoccupied space must decrease and hence the elastic modulus should increase.

During this period, lithium aluminosilicate glasses were prepared and subjected to long periods of ion-exchange in $NaNO_3$ at 325°C, some 150°C below T_g. The decrease of unoccupied space was confirmed by accurate density measurements. When approximately 30% of the Li ions were replaced by Na ions, the elastic modulus was increased by as much as 20%. Thus the theoretical ideas generated in this program were confirmed. This variation of elastic modulus with ion-exchange undoubtedly will open up new avenues o understanding of the glassy state. Ultimately, it should lead to new high modulus glasses via ion-exchange.

b) Structure and Properties of Halide Glasses

Beryllium fluoride glass (BeF_2) is similar to SiO_2 glass in structure.[3]

It is the most well-known "glass-former" for halide glasses. Because fluoride glasses based on BeF_2 have very low refractive indices, they are important as laser materials. There is a great deal of controversy concerning published values of the properties of BeF_2 and BeF_2-based glasses. In the course of this project, very high purity BeF_2 glasses were prepared by distillation. The transmission of BeF_2 glass in the infrared after purification is compared to that of so-called pure BeF_2 glass in Figure 1. The optical properties are dramatically altered. In Figure 2, the ionic conductivity of distilled BeF_2 glass is seen to be a few orders of magnitude lower than that of commonly-reported BeF_2 glass.[4] A new theory was developed to explain the sensitivity of electrical conductivity to water content although water itself nor its ions participate in conduction. Fluorine ions actually are the current carriers. The new theory is based on the "defects" in the glassy network, similar to Frenkel defects in crystals. It was satisfactory when applied to the fluoride glasses.

Some new sodium zinc chlorophosphate glasses were prepared in this period. Infrared absorption studies indicated the presence of mixed ozychloride coordination groups in the glass.

c) New Transparent Glass-Polymer Composites

Sodium borosilicate glasses are readily phase-separated on heat treatment. The sodium borate phase is easily leached away by dilute acid giving rise to a porous silica glass. The pores which are interconnecting can be controlled to have diameters varying between 20A and 1000A. During this period, porous glass having pore diameter of about 40A was impregnated with methyl methacrylate monomer and subsequently polymerized by heating. Preliminary work indicated that a composit comprising of about 40% polymethyl methacrylate and 60% silica glass could be prepared which was totally transparent in the visible. In fact the transmission in the visible was greater than that of

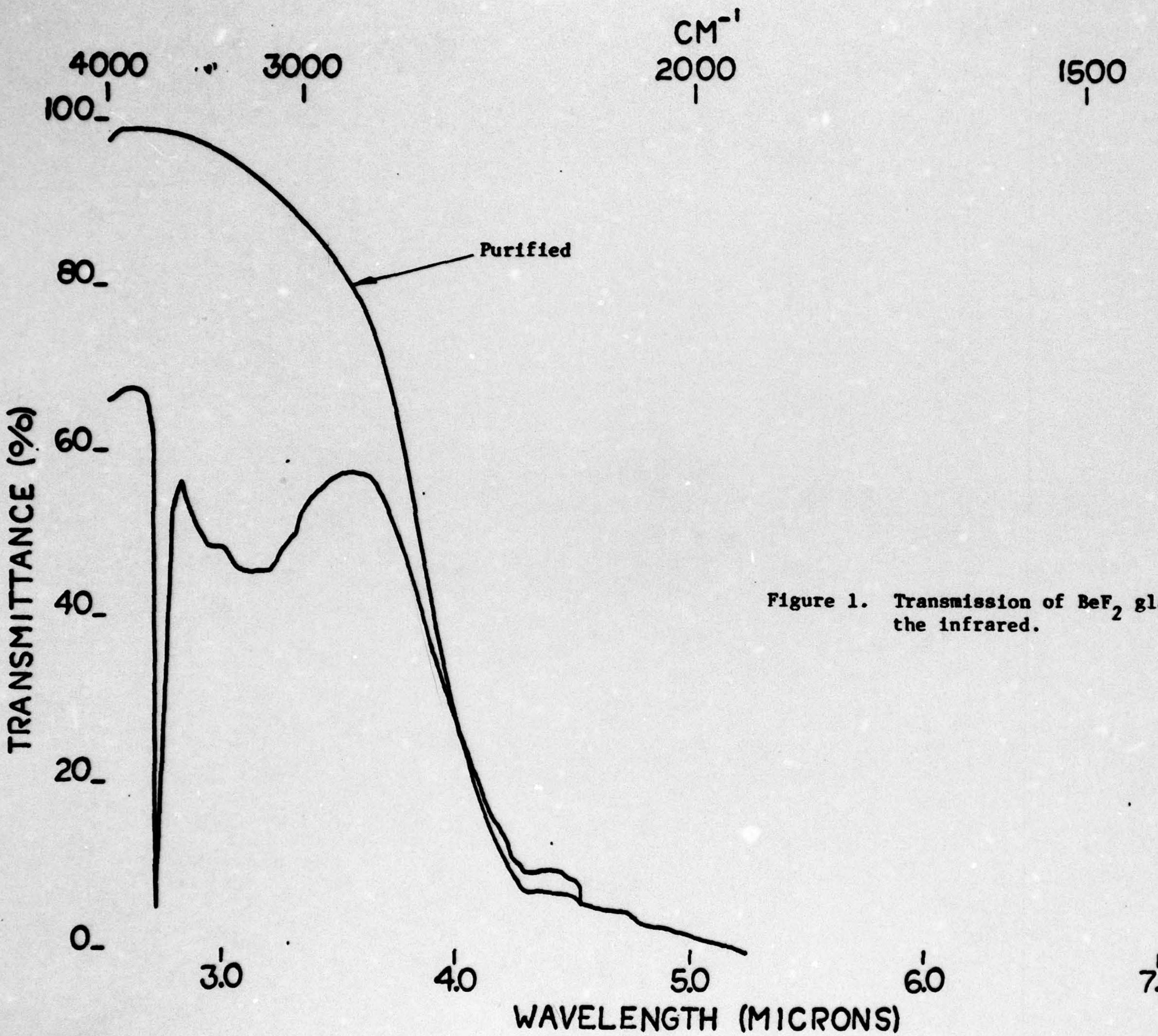

Figure 1. Transmission of BeF_2 glasses in the infrared.

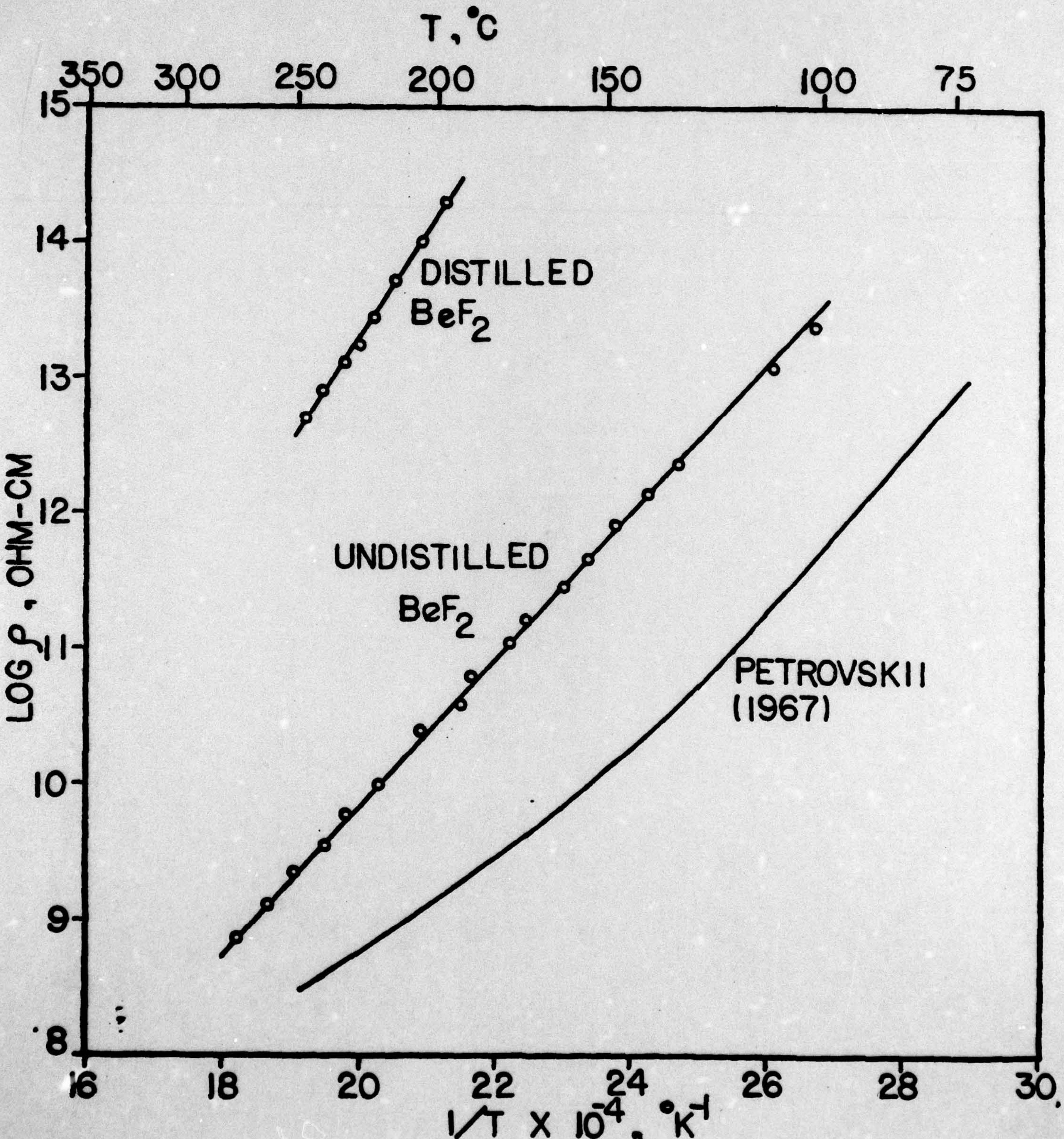

Figure 2. Electrical resistivity of BeF_2 glasses.

common window glass. Further the resultant composite had tensile strength which was higher than that of common silicate glasses although its density was appreciably lower. This remarkable new composite material will be the subject of new research for AFOSR.

4. Relevance of this Program to Air Force

Glass is an important structural, optical and electronic material to the Air Force. The general relevance of a study of the relationship between glass structure and glass properties to the needs of the Air Force is obvious. More specifically, the important implications of the present research are:

a) Improved window materials for aircraft

b) Glasses for laser applications

5. Other Achievements

a) With the collaboration of Dr. D. Ulrich of AFOSR, plans were made and the organization started for an international conference entitled "Frontiers of Glass Science" to be held at UCLA in July, 1980.

b) J.D. Mackenzie was invited to serve on the Organizing Committee of the International Congress on Glass to be held in July, 1980 in Albuquerque, N.M. J.D. Mackenzie was also elected to be Publications Committee Chairman of the International Congress on Glass.

c) J.D. Mackenzie has continued to be Editor-in-Chief of the Journal of Non-Crystalline Solids.

d) The following thesis were awarded to the students named below based on research supported by AFOSR:

C.M. Baldwin, Ph.D.	J. Wakaki, Ph.D.
C.H. Chung, Ph.D.	Jill Ko, M.S.

6. Publications in this Period

"Improvment of Chemical Durability of High Expansion Phosphate Glasses by Ion-Exchange", J. Matls. Sci., 14, 1508-1509 (1979) by K. Matusika and J.D. Mackenzie

"Fundamental Condition for Glass Formation in Fluoride Systems," J. Am. Ceram. Soc., 62, 537-38 (1979) by C.M. Baldwin and J.D. Mackenzie

"Electrical Properties of Semiconducting Glasses", J. Non-Crystalline Solids, 32 91-104 (1979) by L. Murouski, C.H. Chung and J.D. Mackenzie

"Low Expansion Copper Aluminosilicate Glasses", J. Non-Crystalline Solids, 30, 285-92 (1979) by K. Matusita and J.D. Mackenzie

"The Leaching of Phase-Separated Sodium Borosilicate Glasses," J. Non-Crystalline Solids, 31, 377-83 (1979), by A. Makishima, J.D. Mackenzie and J.J. Hammel

"Preparation and Properties of Water-Free Vitreous Beryllium Fluoride," J. Non-Crystalline Solids, 31, 441-45 (1979) by C.M. Baldwin and J.D. Mackenzie

"Application of Glass in Electronics," Glass, 51, 1-14 (1979)

"Ionic Transport and Defect Structure of Vitreous Beryllium Fluoride", J. Non-Crystalline Solids, accepted for publication, by C.M. Baldwin and J.D. Mackenzie

"Infrared Absorption and Structure of Chlorophosphate Glasses," J. Non-Crystalline Solids, accepted for publication by R.M. Almeida and J.D. Mackenzie.

7. Personnel

Dr. J.D. Mackenzie, Principal Investigator

Dr. T. Yoshio, Research Assistant,	1978-79
Mr. J. Wakaki, Research Assistant,	1978-79
Mr. R.M. Almeida, Research Assistant,	1978-79
Miss Jill Ko, Research Assistant,	1978-79

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COMPLETED PROJECT SUMMARY

1. TITLE: Structure and Properties of Glasses

2. PRINCIPAL INVESTIGATOR: Dr. John D. Mackenzie
Materials Department
University of California
Los Angeles, California 90024

3. INCLUSIVE DATES: 1 October, 1978 - 30 September, 1979

4. GRANT NO.: AFOSR-79-0019

5. COSTS AND FY SOURCES: $56,075 FY 79

6. SENIOR RESEARCH PERSONNEL: Dr. T. Yoshio

7. JUNIOR RESEARCH PERSONNEL : J. Wakaki, R.M. Almeida, Jill Ko

8. Publications

"Improvement of Chemical Durability of High Expansion Phosphate Glasses by Ion-Exchange", J. Matls. Sci., 14, 1508-1509 (1979) by K. Matusita and J.D. Mackenzie

"Fundamental Condition for Glass Formation in Fluoride Systems", J. Am. Ceram. Soc. 62, 537-38 (1979) by C.M. Baldwin and J.D. Mackenzie

"Electrical Properties of Semiconducting Glasses", J. Non-Crystalline Solids, Low Expansion Copper Alumo, 30, 285-92 (1979) by K. Matusita and J.D. Mackenzie

"The Leaching of Phase-Separated Sodium Borosilicate Glasses", J. Non-Crystalline Solids, 31, 377-83 (1979) by A. Makishima, J.D. Mackenzie and J.J. Hammel

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"Infrared Absorption and Structure of Chlorophosphate Glasses", J. Non-Crystalline Solids, accepted for publication by R.M. Almeida and J.D. Mackenzie

9. Abstract of Objectives and Accomplishments

The broad objectives of this research are to obtain a greater understanding of the relationships between structure, chemical composition and properties of glasses. From such understanding it was hoped that new glasses of controllable and predictable properties would be prepared.

During this period, it was first predicted and subsequently confirmed that the elastic modulus of oxide glasses was affected by ion-exchange because of the variation of the "unoccupied space" within the glassy network. The elastic modulus of some silicate glasses, was significantly increased by ion-exchange in fused salts. Water entrapped in beryllium fluoride glasses can have a large effect on ionic conductivity despite the fact that fluorine ions are the carriers of current in these glasses. A theory involving a new concept of "defects" in fluoride glasses was satisfactory in explaining the role of water. New composite glasses based on porous silica glass and polymethyl methacryllate with superior optical transmission and high mechanical strengths have been prepared.