DOE
~~COO~~-ER10453.02

Progress Report on

PROPERTIES OF GLASSES WITH HIGH WATER CONTENT

Contract No. DE-AC02-79ER10453

MASTER

for the period

1 March 1980 - 31 January 1981

Minoru Tomozawa
Materials Engineering Department
Rensselaer Polytechnic Institute
Troy, N.Y. 12181

Edward Bruce Watson
Geology Department
Rensselaer Polytechnic Institute
Troy, New York 12181

DISCLAIMER

ABSTRACT

Glasses with high water content were prepared by a hydrothermal process and various properties were measured. The following unique features have been revealed.

1.) Electrical conductivity decreases substantially at first with the addition of water and then increases with the further addition of water. The phenomenon is somewhat similar to the mixed alkali effect.

2.) The glass with high water content is radiation coloration resistant.

3.) With the addition of water, glasses became tougher at room temperature, suggesting the occurence of plastic deformation.

I. INTRODUCTION

This research program was started on June 15, 1979 and the first progress report covering the activity up to the end of February 1980 was submitted last year. In the present report, the subsequent research activity on glasses containing a large amount of water is described.

II. Sample Preparation

Sodium silicate glasses with the composition $Na_2O \cdot 3SiO_2$ were chosen at first because fairly extensive measurements have previously been made on this glass. The "dry" glass was prepared at 1450°C in air by melting a $Na_2CO_3+SiO_2$ mixture in a Pt crucible. A powder of this glass was sealed with various amounts of water in Pt tubes of 5mm O.D. and heated and pressurized in the hydrothermal equipment to obtain homogeneous glasses containing up to 12 wt% water.

Other compositions in the Na_2O-Al_2O_3-SiO_2 and Na_2O-B_2O_3 systems were also prepared to see the effect of the composition modification on properties.

In the hydrothermal method, the size of the specimen is limited. In future practical applications, a larger specimen would be desired. Thus a preliminary investigation was made to prepare a large specimen with high water content by heat-treating a commercial soda-lime glass in wet atmosphere above the glass transition temperature.

III. Results and Discussion

Several properties of $Na_2O \cdot 3SiO_2$ glasses containing a large amount of water were measured. The properties investigated include thermal stability, density, I.R. transmission characteristics, electrical conductivity, dielectric constant, Na diffusion, radiation coloration, hardness, fracture toughness and chemical durability. Among them, the following characteristics are particularly unique and deserve careful evaluation.

1. Electrical Conductivity

Difficulties associated with the small size of the specimen was overcome by reducing the thickness of the specimen and devising a new method of electrode application. An evaporated electrodes were applied on the specimen partly covered by a thin specially prepared washer which is secured by a magnet placed under the specimen. The validity of the method was confirmed using a small specimen of dry glass with known characteristics.

Both a.c. and d.c. electrical characterisitics were determined as a function of water content. A preliminary result showing the large decrease in d.c. conductivity with addition of water was reported in J. Am. Ceram. Soc. and is attached as Appendix I. Subsequently, a complete composition range was investigated and the results shown in Figs. 1-4 were obtained. The initial sharp decrease in d.c. conductivity with increasing water is accompanied by the increase in activation energy and pre-exponential factor, in the same way as in mixed alkali glasses. With the further increase of water, however, the conductivity starts to increase while the activation energy remains nearly constant. Thus the conductivity increase is attributed to the increase of the prexponential factor. This is quite different from the phenomenon commonly observed in mixed alkali glasses and the large amount of molecular water present in the glass appears responsible. Currently the correlation between the electrical characteristic and the amount of various types of water (molecular water, free hydroxyl and hydrogen-bonded hydroxyl) is being sought. The dielectric constant also seems to correlate with the d.c.

conductivity (cf. Fig. 4(A), (B)).

2. Radiation Coloration

Glasses with various amounts of water were subjected to γ-ray radiation of 10^6 rad and the resultant coloration was investigated. Glasses containing high water (> ~1 wt%) remained transparent while the dry glass counterpart became dark. The results are summarized in a note, attached to this report as Appendix II, which will be published in J. Am. Ceram. Soc. This observation suggests, that glasses containing a large amount of water may be useful as radiation shield windows. Currently the mechanisms of this radiation coloration resistance is being investigated.

3. Mechanical Strength

Since specimen size is limited, the fracture toughness was measured using the Vickers indentation method. This involves the measurement of the crack which initiated from the corner of the indent. The preliminary results indicate that as the water content increases, the crack initiation becomes difficult, while hardness decreases. This phenomenon was probably caused by the plastic deformation. This is likely since, in crystalline SiO_2, as water content increases, the mimimum temperature at which plastic deformation takes place becomes lower.

IV. PERSONNEL

Co-Principal Investigators

Minoru Tomozawa
Professor
Materials Engineering Department
Rensselaer Polytechnic Institute

Edward Bruce Watson
Assistant Professor
Geology Department
Rensselaer Polytechnic Institute

Research Assistants

Masasuke Takata
Postdoctoral Research Associate

Joyce Molinelli
Graduate Assistant

John Acocella
Graduate Assistant

V. PUBLICATIONS

1. M. Takata, M. Tomozawa and E.B. Watson, "Electrical Conductivity of $Na_2O \cdot 3SiO_2$ Glasses with High Water Content", J. Am. Ceram. Soc. 63 [11] 710 (1980).

2. M. Takata, M. Tomozawa and T. Takamori, "Dielectric Loss of Micro-structurally Anisotropic Borosilicate Glass" to appear in J. Am. Ceram. Soc.

3. J. Acocella, M. Takata, M. Tomozawa and E.B. Watson, "Radiation Coloration Resistant Glasses with High Water Content". To appear in J. Am. Ceram. Soc.

VI. PRESENTATIONS

1. M. Takata, C. Erwin, J. Acocella, J. Molinelli, M. Tomozawa and E.B. Watson, "Properties of Glasses with High Water Content", Glass Division Am. Ceram. Soc. Fall Meeting, Bedford, PA., October 10, 1980.

2. M. Takata, M. Tomozawa and T. Takamori, "Dielectric Loss of Micro-Structurally Anisotropic Borosilicate Glasses", Glass Division Amer. Ceram. Soc. 1980 Fall Meeting, October 10, 1980.

3. M. Takata, "Properties of Glasses with High Water Content", Condensed Matter Physics Seminar, Dept. of Physics, RPI, November 10, 1980.

FIGURES

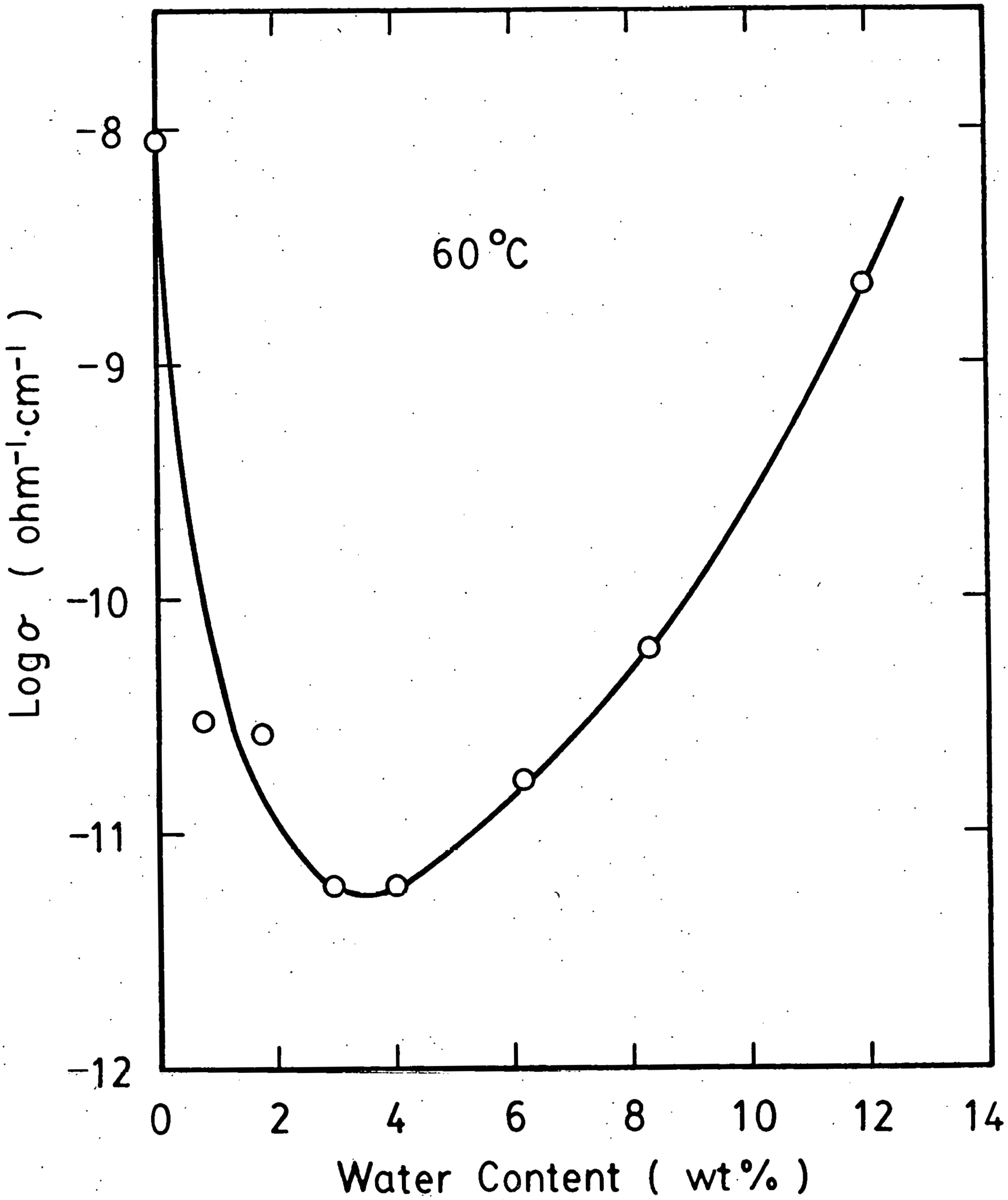


Figure 1: d.c. conductivity of $Na_2O \cdot 3SiO_2 \cdot nH_2O$ glasses at 60°C as a function of water content.

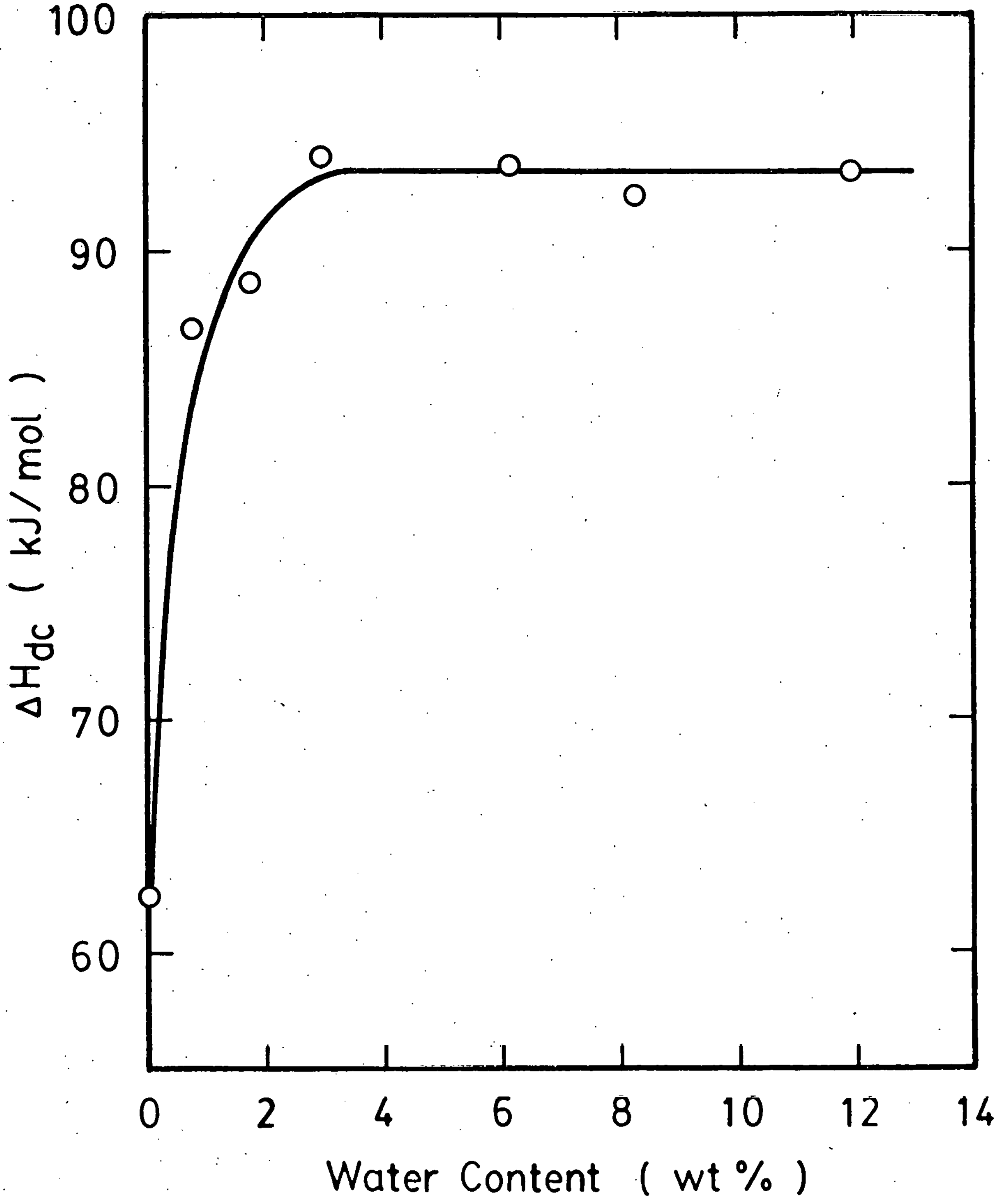


Figure 2: Activation energy of d.c. conduction for $Na_2O \cdot 3SiO_2 \cdot nH_2O$ glasses as a function of water content.

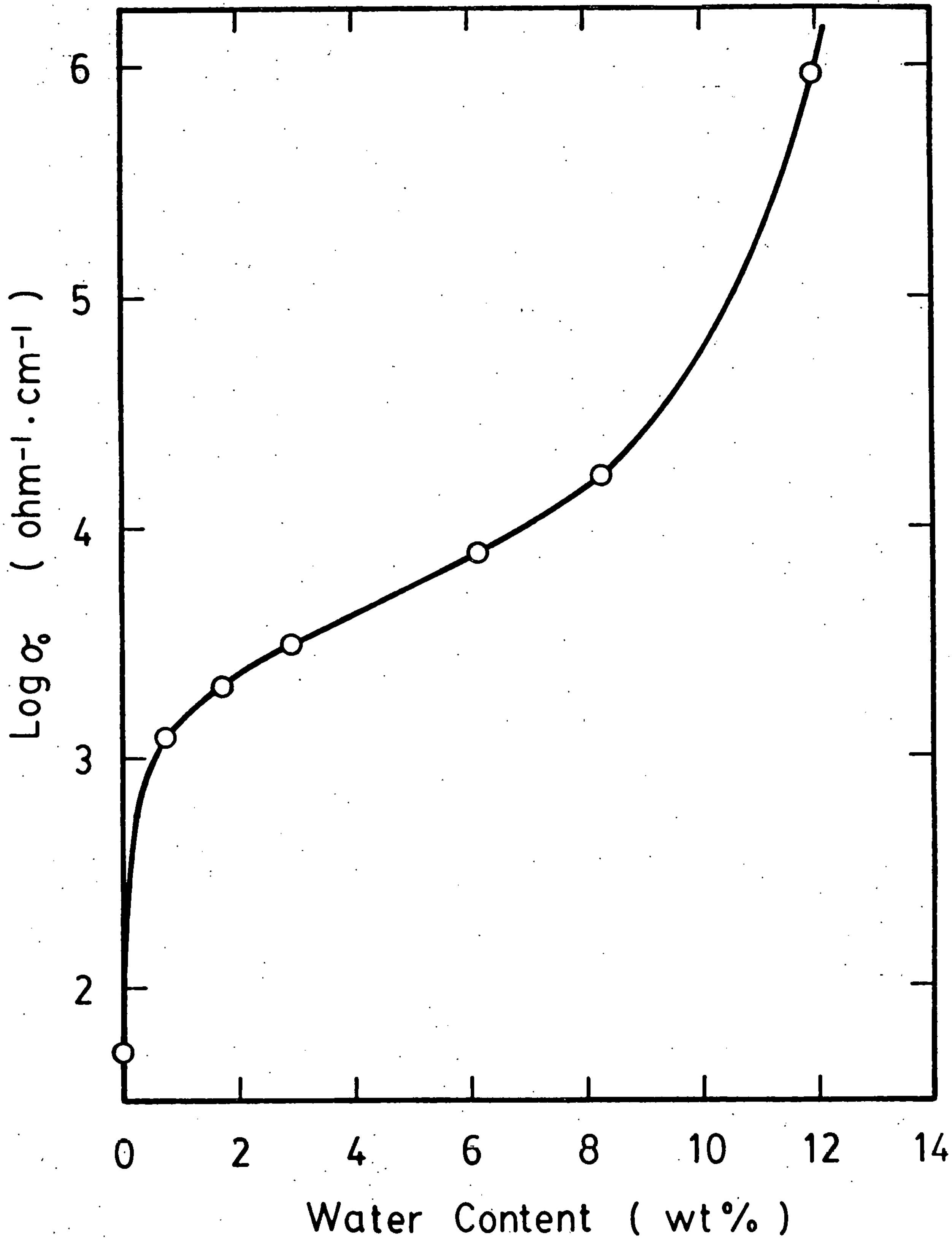


Figure 3: Pre-exponential factor of d.c. conductivity of $Na_2O \cdot 3SiO_2 \cdot nH_2O$ glasses as a function of water content.

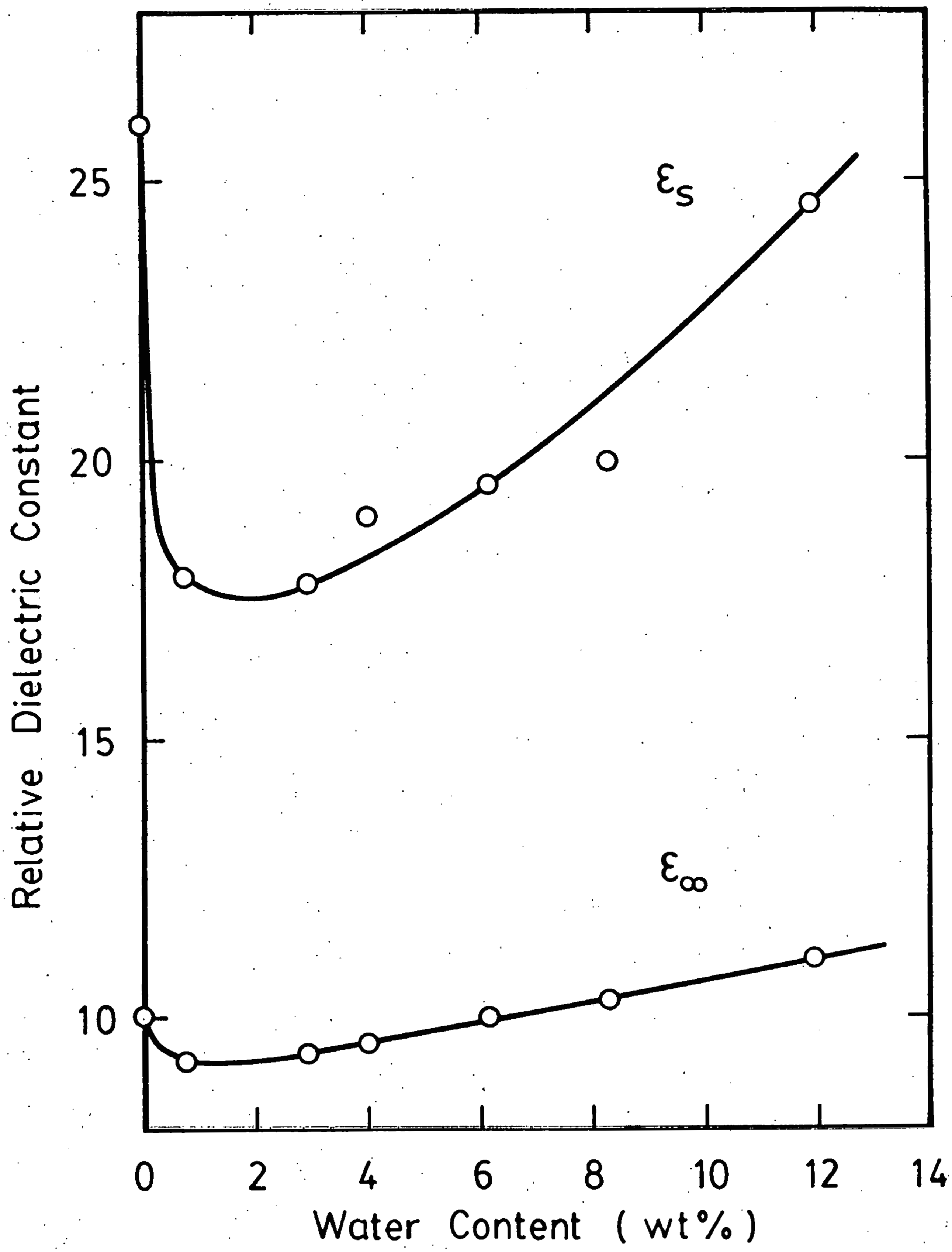


Figure 4(A): Dielectric constants of $Na_2O \cdot 3SiO_2 \cdot nH_2O$ glasses as a function of water constant.
ε_S: static dielectric constant. ε_∞: High frequency dielectric constant.

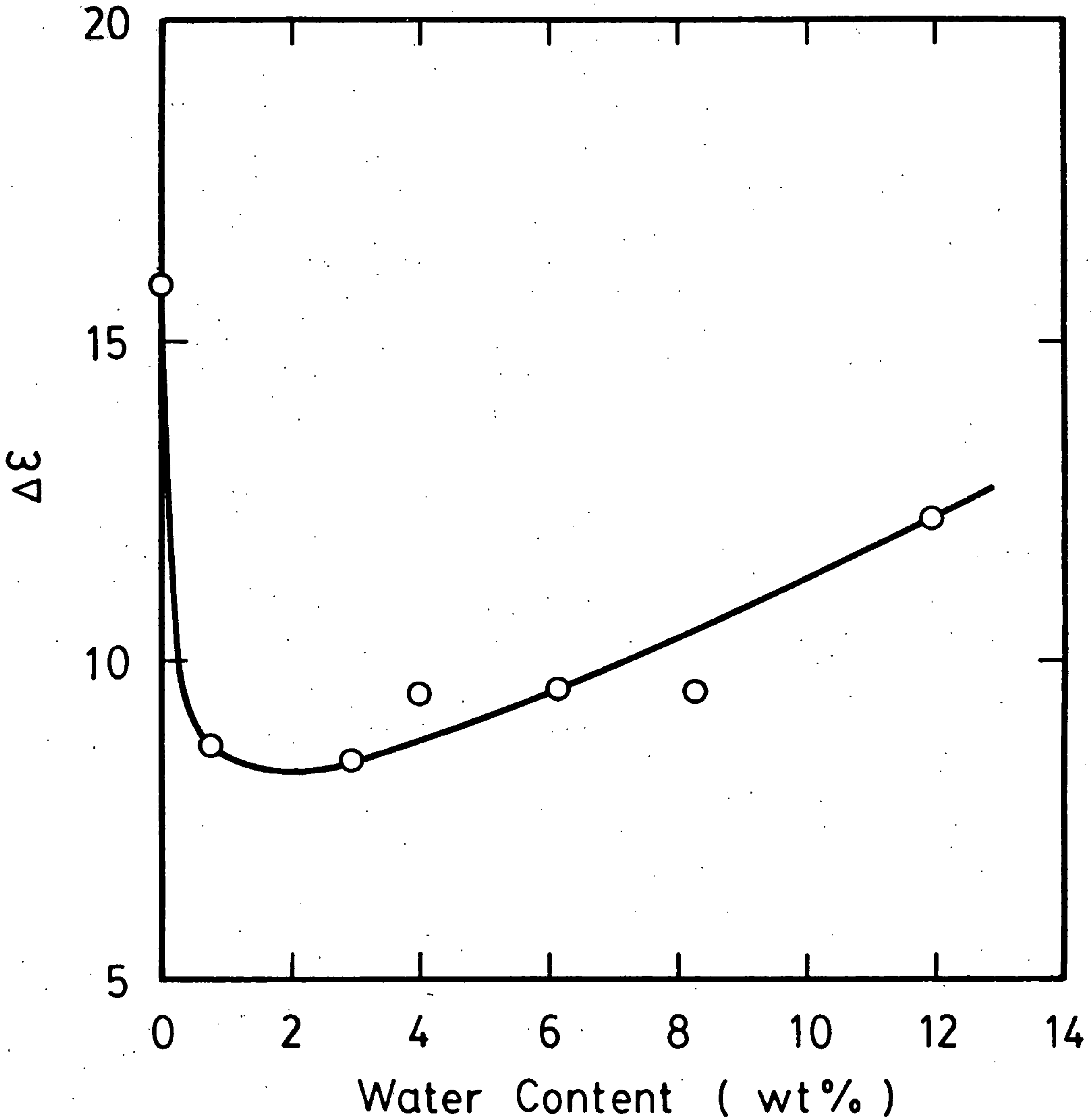


Figure 4(B): Dielectric strength Δε of $Na_2O \cdot 3SiO_2 \cdot nH_2O$ as a function of water content. $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$

APPENDIX I

removed
Reprint

APPENDIX II

REVISED 1/9/81

Appendix II

Radiation Coloration Resistant Glasses With High Water Content

J. Acocella, M. Takata, M. Tomozawa
and E.B. Watson

Rensselaer Polytechnic Institute
Troy, New York 12181

Abstract

Radiation coloration resistant glasses were prepared by incorporating a large amount of water into dry glasses under hydrothermal conditions. After γ -ray irradiation of 10^6 rad, the glasses remained transparent.

Most glasses turn brown or black when subjected to X-rays or γ-rays. There are, several indications[1-8] that dissolved water in glass may influence radiation coloring. In these previous investigations, however, the water content of the glass was comparatively low, usually in the range of a few ppm to a few hundred ppm. Therefore, the actual effect of water can be obscured by slight changes in other components.

In order to unequivocally evaluate the effects of dissolved H_2O in the present research, a large quantity of water (2~10 wt%) was incorporated into $Na_2O \cdot 3SiO_2$ and Na_2O-Al_2O_3-SiO_2 glasses by a hydrothermal pressure method, and their coloration by γ-ray radiation was compared with that of the corresponding dry glasses.

The details of the sample preparation and the determination of high water concentrations were described previously by Takata et al[9]. However, in the present experiment the melting time at 800°C and 200 MPa (2kbar) was extended to 24 h in order to ensure uniform distribution of water in the glass.

Samples with dimensions of 3mmX9mmX.5mm were irradiated at room temperature with a ^{60}Co γ-source to a total dose of $1X10^6$rad. In contrast to the severe darkening of dry glasses in this γ flux, the glasses containing water remained transparent. One example is shown in fig. 1, in which a $Na_2O \cdot 3SiO_2$ glass specimen containing 2.2 wt% water is compared with dry glass which was found to contain ~0.05 wt% H_2O. The transmission spectra of these glasses in the visible and u.v. range were obtained before and 10 days after irradiation using an American Instrument Co. DW-2 UV-VIS Spectrophotometer and are shown in fig. 2 and fig. 3. It is clear from figures 2 and 3 that the transmission of the dry glass decreases considerably by γ-ray irradiation while that of the glass containing a large amount of water remains practically unchanged. The difference is most likely due to water in the glass. The high pressure employed in the preparation of glasses with high water contents cannot be responsible since the high pressures are known to increase the absorption[10] rather than decrease it. It is known that the transmission characteristics change with the time during and immediately after irradiation. In the present experiment, the transmission characteristics, which appear to be steady state, were measured approximately 10 days after irradiation during which time the specimens were kept in a desiccator at room temperature and in the dark.

At present, the exact mechanism by which water suppresses the radiation colorating is not clear. It is possible that a mechanism similar to that proposed by Faile and Roy[11] for SiO_2 glass impregnated with H_2 is applicable here. Namely, water in glass may be combining with color centers, producing colorless Si-OH. The details of the phenomenon are under investigation.

Acknowledgements

The authors would like to thank L.M. Lawe of HANSCOM A.F.B. for performing the sample irradiations. This research has been supported by DOE Contract DE-AC02-79ER10453.

REFERENCES

1. George W. Arnold and W. Dale Compton, "Radiation Effects in Silica At Low Temperatures", Phys. Rev., 113 [4] 802-811 (1959).

2. V. Garino Canina and M. Priqueler, "Diffusion of Protons in $SiO_2 + Al_2O_3$ Glass in An Electrical Field", Physics and Chemistry of Glasses, 3 [2], 43-45 (1962).

3. E.J. Friebele, R.J. Ginther, and G.H. Sigel, Jr., "Radiation Protection of Fiber Optic Materials: Effects of Oxidation and Reduction", Appl. Phys. Lett., 24 [9] 412-414 (1974).

4. E.J. Friebele and D.L. Griscom, p. 303-312 in Treatise on Material Science and Technology, Vol. 17: Glass II. Edited by M. Tomozawa and R.H. Doremus. Academic Press, New York, 1979.

5. R.A. Weeks and E. Lell, "Relation Between E'Centers and Hydroxyl Bonds In Silica", J. Appl. Phys., 35 [6] 1932-38 (1964).

6. E.J. Friebele, R.E. Jaeger, G.H. Sigel and M.E. Gingerich, "Effect on Ionizing Radiation on the Optical Attenuation in Polymer-Glad Silica Fiber-Optic Waveguides", Appl. Phys. Lett., 32 [2] 95-97 (1978).

7. E.J. Friebele, M.E. Gingerich, and G.H. Sigel, Jr., "Effect of Ionizing Radiation on the Optical Attenuation in Doped Silica and Plastic Fiber-Optic Waveguides", Appl. Phys. Lett., 32 [10] 619-621 (1978).

8. E.J. Friebele, P.C. Schultz and M.E. Gingerich, "Compositional Effects on the Radiation Response of Ge-Doped Dilica Core Optical Fiber Waveguides", to be published.

9. M. Takata, M. Tomozawa, and E.B. Watson, "Electrical Conductivity of $Na_2O \cdot 3SiO_2$ Glasses with High Water Content", J. Am. Ceram. Soc., 63 [11-12] to be published.

10. T. Yawamoto, S. Sakka and M. Tashiro, "Effect of Pressure on Radiation Induced Color Centers in Silicate Glasses", J. Non-Cryst. Solids 1 441-459 (1969).

11. S.P. Faile and D.M. Roy, "Mechanism of Color Center Destruction in Hydrogen Impregnated Radiation Resistant Glasses", Mat. Res. Bull., 5 385-390 (1970).

Figure Captions

Figure 1: Dry $Na_2O \cdot 3SiO_2$ and $Na_2O \cdot 3SiO_2$ + 2.2 wt% H_2O 10 days after irradiation with $1X10^6$ rad γ-ray at room temperature. Thickness of specimens is approximately 0.5 mm.

Figure 2: % Transmission vs. Wavelength: Dry $Na_2O \cdot 3SiO_2$ before and 10 days after irradiation. Thickness of the specimens is approximately 0.5 mm.

Figure 3: % Transmission vs. Wavelength: $Na_2O \cdot 3SiO_2$ + 2.2 wt% H_2O before and 10 days after irradiation. Thickness of the specimens is approximately 0.5 mm.

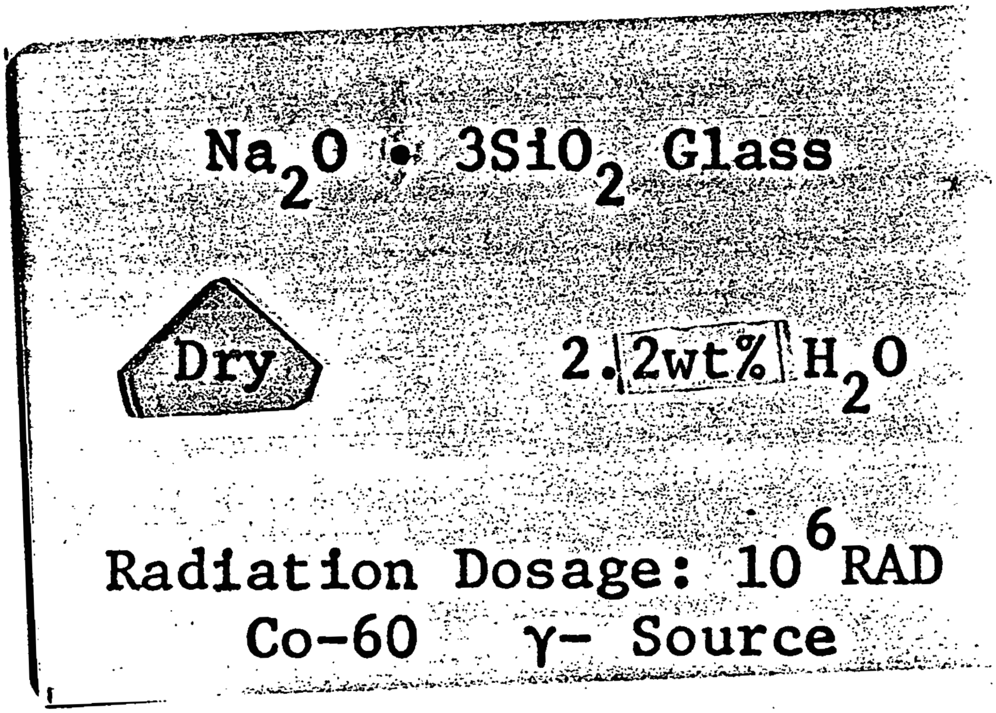

Na2O • 3SiO2 Glass
Dry
2.2wt% H2O
Radiation Dosage: 10^6 RAD
Co-60 γ- Source

Figure 1

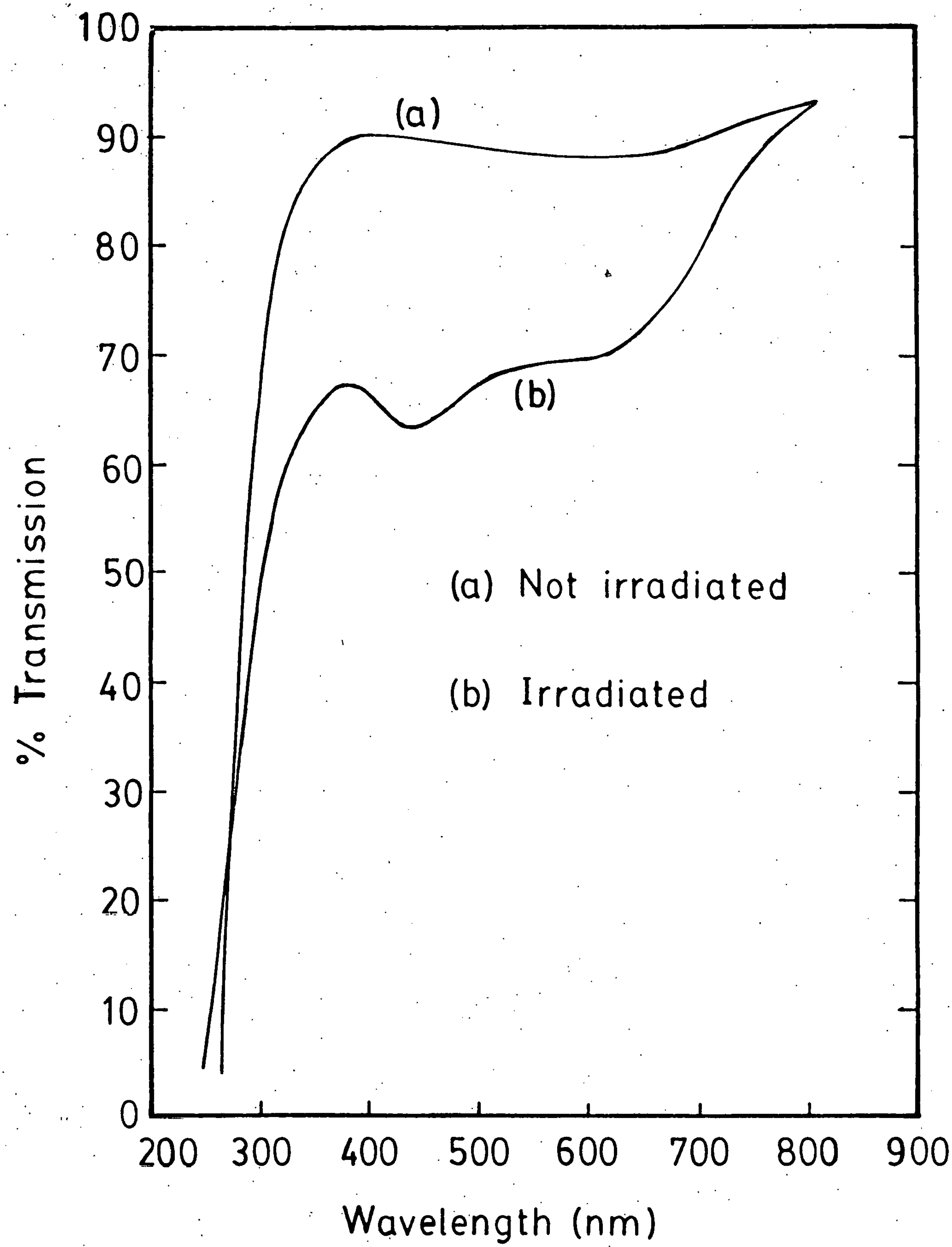
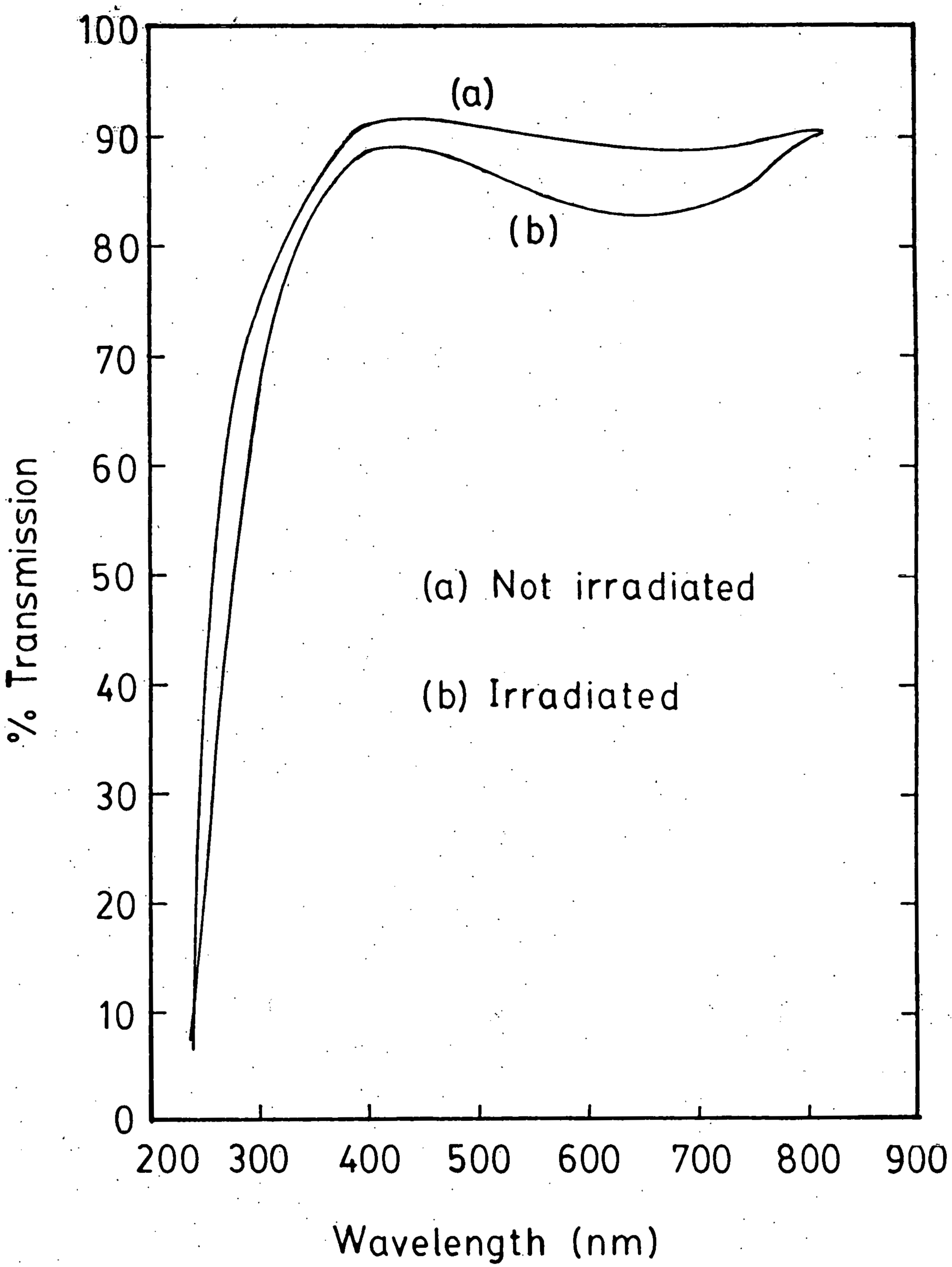

100
90
80
70
60
50
40
30
20
10
0
% Transmission
(a)
(b)
(a) Not irradiated
(b) Irradiated
200
300
400
500
600
700
800
900
Wavelength (nm)

figure 2



100
90
80
70
60
50
40
30
20
10
0
% Transmission
(a)
(b)
(a) Not irradiated
(b) Irradiated
200
300
400
500
600
700
800
900
Wavelength (nm)

figure 3