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INTERIM REPORT

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ULTRAPURE GLASS OPTICAL WAVEGUIDE
 DEVELOPMENT IN MICROGRAVITY
 BY THE SOL-GEL PROCESS
 (JPL CONTRACT 955710)

to

JET PROPULSION LABORATORY
 CALIFORNIA INSTITUTE OF TECHNOLOGY



January 15, 1981

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by

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February 6, 1981

JET PROPULSION LABORATORY
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Attention: Mr. M. H. Jacobs, Senior Contracts Administrator

JPL Contract 955710
Ultrapure Optical Waveguide
Development in Microgravity
by the Sol-Gel Process

Gentlemen:

Battelle's Columbus Laboratories is pleased to submit ten (10) copies of our Interim Report on Contract 955710. The report includes work performed in the period April 10, 1980 through November 10, 1980. This completed and approved document includes changes and/or corrections supplied by the JPL technical monitor in a letter to BCL dated December 5, 1980.

Inasmuch as a contract extension has been negotiated for the FY-1981 for Contract 955710, the designation "Interim Report" has been substituted for the designation "Final Report".

If there are any questions, please do not hesitate to contact Dr. S. P. Mukherjee at (614) 424-4053 or Mr. F. J. Jelinek at (614) 424-7472.

Sincerely,

S. P. Mukherjee

Dr. S. P. Mukherjee, Principal Investigator

Mr. F. J. Jelinek, Project Manager

SPM/FJJ/pap

Enc. (10)

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY.	3
EXPERIMENTAL WORK AND RESULTS.	5
Choice of Composition	5
Preparation of Gels	6
Starting Compounds	6
Gel Preparation Procedures	7
Thermal Treatment of Gels	8
Characterization of Gels.	9
Color of Gels.	9
Carbon Content	9
Crystallinity.	9
Surface Areas.	12
Conversion of Gels to Glasses by Melting.	15
Characterization of Glasses	15
Infrared Spectroscopic Studies	15
Raman Spectroscopic Studies.	15
Treatment for the Removal of Hydroxyl Groups from the Gels.	21
Experiment 1	21
Experiment 2	22
Experiment 3	22
DISCUSSION	22
CONCLUSIONS.	25
ACKNOWLEDGEMENTS	26

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

	<u>Page</u>
Table 1. Color of Gels After Heat Treatment	10
Table 2. Crystallinity of Gels After Various Thermal Treatments	11
Table 3. Surface Areas of the Gels Prepared by Different Procedures After One Half Hour Heat Treatment at Different Temperatures.	13
Table 4. Surface Areas of Gel Samples After Different Thermal Treatments	14
Table 5. Effect of Time and Temperature on the Removal of Residual Carbon During the Melting of Gels Prepared by Procedure I.	16
Table 6. Effect of Time and Temperature on the Removal of Residual Carbon During the Melting of Gels Prepared by Procedure II	17
Table 7. Effect of Time and Temperature on the Removal of Residual Carbon During the Melting of Gels Prepared by Procedure III.	18
Table 8. Characteristics of the IR Absorption Bands Due to Si-O-Si Stretching of Different Glasses	19
Table 9. Melting Histories of the Samples for the Raman Spectroscopic Studies.	20

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY

from

BATTELLE
Columbus Laboratories

January 15, 1981

INTRODUCTION

The melting of glass in a terrestrial environment involves an obstacle to maintaining low purity levels due to contamination by container walls, a problem which can be alleviated by containerless melting in the space environment. The ultimate objective of the present research program is to take advantage of the containerless melting of glasses in space for the preparation of ultrapure homogeneous glass for optical waveguides. However, the homogenization of the glass using conventional raw materials is normally achieved on earth either by the gravity induced convection currents or by the mechanical stirring of the melt. Because of the absence of gravity induced convection currents, the homogenization of glass using conventional raw materials will be difficult in the space environment.

Multicomponent, homogeneous, noncrystalline oxide gels can be prepared by the sol-gel process and these gels are promising starting materials for melting glasses in the space environment. The sol-gel process referred to here is based on the polymerization reaction of alkoxy-silane with other metal alkoxy compounds or suitable metal salts. Many

of the alkoxysilanes or other metal alkoxides are liquids and thus can be purified by distillation. The use of gels offers several advantages such as high purity and lower melting times and temperatures. Hence, the present research program aims at the utilization of the sol-gel process for the preparation of multicomponent ultrapure glass batches for subsequent containerless melting of the batches in space to prepare glass blanks for optical waveguides.

Prior to "space readiness", however, several critical control points must be carefully evaluated on earth. Hence the present ground based program comprises two major phases; Phase 1 and Phase 2.

Phase I involves the following activities:

- Selection of the best multicomponent glass system suitable for optical waveguides
- Choice of composition in a particular system
- Preparation of gels in the chosen multicomponent system (with reagent grade chemicals) by different procedures
- Thermal treatment of gels for removal of volatiles and water
- Characterization of gels
- Melting of gels prepared by different procedures
- Characterization of the resulting glasses in terms of properties relevant to optical waveguide applications.

Phase 2, to be initiated in a follow-on effort, plans to concentrate on the following activities:

- Preparation of ultrapure gels by using ultrapure chemicals and a class 100 clean room
- Melting of ultrapure gel pellets using both a container and containerless melting
- Characterization of glasses in terms of trace level transition metal impurities and absorptive losses.

Some of the activities of Phase 1 were performed during the year 1979 (JPL Contract 955361) and have been reported in the Final Report

to Jet Propulsion Laboratory, February 22, 1980. The present Report describes the further activities of work and concentrated on the following activities

- (a) Preparation of gels in the alkali borosilicate system by different procedures developed during the initial period of the program
- (b) Evaluation of the physico-chemical nature of gels prepared by different procedures
- (c) Investigations of the structure of glasses obtained by the melting of the gels prepared by different procedures
- (d) Effects of the melting history (e.g., time and temperature) on the structure of the glasses obtained from the gels
- (e) Thermal treatment for the removal of hydroxyl groups from the gels.

SUMMARY

The results of the present work can be summarized as follows:

- (1) Gels in the alkali borosilicate system were prepared by three different procedures. The composition selected was a high alkali content one, being outside the metastable liquid-liquid immiscibility zone.
- (2) Three preparation procedures using three different sources of alkali oxide were used. The sources of alkali oxide were sodium methylate, sodium nitrate and sodium acetate. It is evident from the results that the chemistry of the gelling process is dependent on the chemical nature of the alkali compound.
- (3) The removal of organic groups from the gels prepared by different procedures was investigated. The carbon contents of the gels prepared by different procedures and after firing at 600 C varied from 0.1% to 0.6% (by weight). The minimum was with the gels prepared by the procedure using sodium nitrate as the alkali

oxide source. The maximum was with the gels prepared by the procedure using sodium acetate as the alkali oxide source.

- (4) Results of the surface area measurements of the gels indicate that the porosity of the gels prepared by the different procedures was different and the closing of the pores as a function of temperature was also different with different gels.
- (5) The gels prepared by two procedures using sodium methyrate and sodium acetate were noncrystalline and no crystallinity developed on thermal treatment at 600 C for 40 hours. The gels prepared by procedures using sodium nitrate were crystalline due to the presence of residual sodium nitrate which reacts and decomposed eventually during the thermal treatment at higher (approximately 600 C) temperatures.
- (6) The elimination of residual carbon from the glass during the melting of gels was investigated. The retention of carbon in the gel is dependent on the gel preparation procedure. Subsequent elimination of carbon from the glass is a function of time, temperature and ambient atmosphere of melting. The elimination was most rapid with the gels prepared by the procedure using sodium nitrate as alkali oxide source, and was most sluggish with the gels prepared by the procedure using sodium acetate as alkali the source.
- (7) Molecular structures of glasses obtained by melting the gels prepared by the different procedures at a lower temperature (≤ 1000 C) were not identical. However, the melting at 1200 C or above is sufficient to give equilibrium (or nearly so) in the melts from the different gels.

- (8) Preliminary experimental procedures were developed for the removal of hydroxyl groups from the porous gels by treatment with thionyl chloride vapor carried by dry oxygen.

EXPERIMENTAL WORK AND RESULTS

The experimental results of the present work have been divided into the following activities:

- Choice of composition
- Preparation of gels
- Thermal treatment of gels
- Characterization of gels
- Melting of gels and conversion to glasses
- Characterization of glasses
- Treatment for the removal of hydroxyl groups from the gel powders.

Choice of Composition

The objective of the initial work was to develop the gel preparation procedures and to characterize the glasses obtained from the gels prepared by the different procedures. A composition containing a high proportion of alkali oxide and being outside the metastable liquid-liquid immiscibility zone was selected for the present study. The composition was as follows (in weight percent) $\text{SiO}_2:60$; $\text{B}_2\text{O}_3:15$; $\text{Na}_2\text{O}:25$.

The composition with high alkali content was chosen because it is presumed that the preparation of noncrystalline homogeneous gels having high alkali content would encounter more difficulties. The difficulties would be associated primarily with the nonuniform distribution of Na^+ ions. The mechanism of fixation of Na^+ ions in the gel-network is not understood. If it is by an ion-exchange mechanism, then the exchange of high concentration of Na^+ ions would be difficult. If we can solve

the problems associated with the preparation of gels having high alkali oxide content, we will have less problems with the compositions having low alkali content.

When the gel preparation process and the relation of gel structures to the glass structures are understood to some extent, a series of compositions suitable for getting low loss glasses could be investigated.

Preparation of Gels

The development of the gel preparation procedures has been considered in terms of several factors which are important for fulfilling the objectives of the present research program. Hence, the following factors were considered during the gel development preparation procedures:

- Chemical nature of the starting compounds and the purity attainable with the starting compounds
- Homogeneity of the solution and the gelling rates
- Removal of organics
- Crystallinity of gels.

Starting Compounds

The following starting compounds were used as sources of different oxides.

Oxide	Source
SiO ₂	Tetraethyl Orthosilicate
	Tetraethyl Orthosilicate Hydrolysate
B ₂ O ₃	Boric Acid
	Trimethyl Borate
Na ₂ O	Sodium Nitrate
	Sodium Acetate
	Sodium Methylate

Gel Preparation Procedures

Several preparation procedures were developed during the initial period (Final Progress Report, JPL Contract 955361) of this program. Three preparation procedures using three different sources of Na_2O were selected from the procedures developed earlier. However, some modifications of the procedures were made during the present work. The preparation procedures are described below.

Procedure I. Starting Compounds: Tetraethyl Orthosilicate
Boric Acid
Sodium Methylate

Tetraethyl orthosilicate was mixed with about 1/2 its volume of anhydrous ethanol. The solution was heated to 40 C, and after 10 minutes tetraethyl orthosilicate was partially hydrolysed with a small proportion of acidified water [2 mol H_2O /mol of $\text{Si}(\text{OC}_2\text{H}_5)_4$]. The pH of the solution was five after the addition of acidified water. A small volume of acetylacetone (3 ml/100 ml of $\text{Si}(\text{OC}_2\text{H}_5)_4$) was added after the addition of acidified water. After stirring the solution for 1/2 hour, boric acid dissolved in boiling methanol (30 g/100 ml) was added to the solution. The pH of the solution was about six. After 1 hour, sodium methylate dissolved in methanol was added to the mixture. The pH increased to about 10. The solution was stirred for 45 minutes. After 45 minutes, a mixture of water and ethanol (1:4 ratio) was added to the solution to introduce more water for further hydrolysis and gelation. The amount of water added was 5.8 mols per mol of $\text{Si}(\text{OC}_2\text{H}_5)_4$. The solution gelled within 5 minutes on addition of the alcohol water mixtures.

Procedure II. Starting Compounds: Tetraethyl Orthosilicate
Boric Acid
Sodium Nitrate

Tetraethyl orthosilicate was mixed with about 1/2 its volume of anhydrous ethanol. The solution was heated to approximately 40 C. After 5 minutes, a requisite amount of water acidified with dilute HCl was added for the partial hydrolysis of tetraethyl orthosilicate. After stirring for 1/2 hour, boric acid dissolved in methanol (30 gms/100 ml) was added

to the solution. The solution was stirred for about 1 hour. Finally, a dilute aqueous solution of sodium nitrate was added to the mixture. The total amount of water added with the sodium nitrate was several times the amount of water required for the complete hydrolysis of tetraethyl orthosilicate. The proportion of water was 20 mols per mol of $\text{Si}(\text{OC}_2\text{H}_5)_4$.

Procedure III. Starting Compounds: Tetraethyl orthosilicate
Trimethyl Borate
Sodium Acetate

Tetraethyl orthosilicate was mixed with 1/2 its volume of anhydrous ethanol. The mixture was heated to 40 C, and was hydrolysed in excess water in the presence of an acid catalyst with a pH of approximately two. The amount of water added was about 11 mols per mol of $\text{Si}(\text{OC}_2\text{H}_5)_4$. After stirring for 1/2 hour, trimethyl borate was added and the mixture was stirred for 45 minutes. Finally, a sodium acetate solution was added rapidly to the solution with continuous stirring. The gelation took place after 1/2 hour.

Thermal Treatment of Gels

The thermal treatment procedure used for the removal of organics consisted of heating in steps and a slow rate of heating.

The thermal treatment procedure consisted of the following steps:

- (1) Drying in air under an infrared lamp (~ 60 C) for 2 to 3 days.
- (2) Drying in an air oven at approximately 150 C for 48 to 60 hours.
- (3) Heating from 150 C to 600 C at the rate of 10 C/hour.
- (4) Holding at 600 C for about 20 hours.

It was observed that the spraying of water during the initial thermal treatment under the infrared lamp was beneficial for the removal of organic groups during the firing cycle. Initial thermal treatments of "as prepared" gels in a humidity chamber were also beneficial for the removal of organic groups.

Characterization of Gels:

The characterization of gel powders were carried out after the thermal treatments. The following aspects of the physico-chemical nature of the gels were examined.

- Color after the thermal treatment
- Carbon content
- Crystallinity
- Specific surface areas.

Color of Gels

The results of thermal treatments at various temperatures and times are summarized in Table 1. It is evident from the results that the removal of organics from the gels is related to the gel preparation procedure as well as to the thermal treatment procedures.

Carbon Content

The total carbon content of gels prepared by different procedures and heat treatment at 600 C for 40 hours were analyzed. The results are given below.

<u>Gel Preparation Procedure</u>	<u>Total Carbon Content (wt. %)</u>
I	0.1
II	0.1
III	0.6

Crystallinity

Gel samples after thermal treatments of 600 C for different time periods were examined by x-ray powder pattern techniques. Results are given in Table 2.

TABLE 1. COLOR OF GELS AFTER HEAT TREATMENT

Gel Preparation Procedure	Heat Treatment	Appearance
I	150 C for 48 hours	Tan
I	150 C for 48 hours and 600 C for 5 hours	Grey
I	150 C for 48 hours 600 C for 40 hours	Grey
II	150 C for 48 hours	White
	150 C for 48 hours and 600 C for 5 hours	White
	150 C for 48 hours 600 C for 40 hours	White
III	150 C for 48 hours 600 C for 40 hours	Black
	150 C for 48 hours 600 C for 5 hours	Black with grey particles
	150 C for 48 hours 600 C for 40 hours	"

TABLE 2. CRYSTALLINITY OF GELS AFTER VARIOUS THERMAL TREATMENTS

Gel Preparation Procedure	Thermal Treatment	Crystallinity
I	13 Hours at 500 C	Noncrystalline
I	24 Hours at 500 C	Noncrystalline
I	2 Hours at 600 C	Noncrystalline
I	40 Hours at 600 C	Noncrystalline
II	After Air Dryup	Crystalline, (Due to NaNO_3)
II	2 Hours at 500 C	Crystalline
II	2 Hours at 600 C	Crystalline
II	40 Hours at 600 C	Crystalline
III	13 Hours at 500 C	Noncrystalline
III	24 Hours at 500 C	Noncrystalline
III	2 Hours at 600 C	Noncrystalline
III	40 Hours at 600 C	Noncrystalline

Surface Areas

The surface area of the gels prepared by different procedures were measured on a micrometric instrument through a range of temperatures to get an idea about the change of surface area with temperature.

Two sets of experiments were performed to study the change of surface area as a function of temperature. In the first series of experiments, the surface areas were measured on a micrometric instrument through a range of temperatures in-situ. The gels were held at each rising temperature for 1/2 hour before the measurement of surface areas. The heating was done while the samples were under the micrometric instrument. In this series of experiments, the fresh gel sample was heat treated inside the micrometric instrument and was evacuated after the heat treatment, and subsequently, the surface area was measured. Consequently, the surface was not exposed to the atmosphere after the heat treatment and surface pores were cleaned under vacuum after the volatilization of the solvents. Moreover, the time was short, so the time may not have been long enough for reaching the equilibrium surface area at that temperature, because at higher temperatures, the formation of pores as well as the closing of pores might occur simultaneously. Results of the first set of experiments are shown in Table 3.

In the second series of experiments, the gels were heat treated at different temperatures for different time periods in a furnace under air atmosphere. The samples were then taken out, and stored in atmospheric conditions. Subsequently, the surface area of the heat treated gels were measured. Moreover, the period of heat treatment was longer than that of the first set of experiments. Consequently, the heat treatment at higher temperatures for longer time periods might have caused opening as well as closing of the pores. Results of these experiments are shown in Table 4.

TABLE 3. SURFACE AREAS OF THE GELS PREPARED BY DIFFERENT PROCEDURES AFTER ONE HALF HOUR HEAT TREATMENT AT DIFFERENT TEMPERATURES

Gel Preparation Procedure	Temperature of Treatment	Surface Area m^2/gm
I	150 C	40.00
I	300 C	42.00
I	500 C	<u>0.00</u>
II	150 C	6.00
II	300 C	6.00
II	400 C	6.00
II	500 C	<u>0.00</u>
III	150 C	2.00
III	300 C	25.00
III	400 C	100.00
III	500 C	11.00

TABLE 4. SURFACE AREAS OF GEL SAMPLES AFTER DIFFERENT THERMAL TREATMENTS

Gel Preparation Procedure	Heat Treatment Temperature (C)	Period of Heat Treatment (Hours)	Surface Area (m ² /gm)
I	200	2	15
I	200	4	22
I	250	2	15
I	250	4	13
I	250	6	15
I	300	2	14
I	300	4	15
I	300	6	6
II	200	2	30
II	200	4	33
II	275	2	33
II	275	4	34
II	275	6	21
II	350	2	20
II	350	4	1
II	350	6	0.37
III	200	2	40
III	200	6	51
III	300	2	38
III	300	4	46
III	400	2	49
III	400	4	50
III	400	6	42

Conversion of Gels to Glasses by Melting

The gels prepared by different procedures were heat treated up to 500 C to remove organic matters and were subsequently melted at 1000 C to obtain clear glass by eliminating residual carbons. The results are summarized in Table 5, 6, and 7.

Characterization of Glasses

The molecular structure of the glasses obtained from the gels prepared by different methods were investigated by Infrared Spectroscopy and Raman Spectroscopy.

Infrared Spectroscopic Studies

The infrared spectra of the glasses were taken by the KBr pellet technique, the results showing the change in the position of the absorption band due to Si-O-Si stretching (ν cm^{-1}) are given in Table 8. In this case, the same gel sample was heat treated at three or more subsequent temperatures; in other words, the sample heat treated at 500 C already had thermal treatments below 500 C. Moreover, the time given might not be enough for the equilibrium to be reached at that temperature.

Raman Spectroscopic Studies

The Raman spectra of glass samples in the fiber form were measured in the region 200 to 1300 cm^{-1} . This region contains the characteristic vibrations of the glass structure. The Raman spectroscopic measurement was done at the Materials Research Laboratory of the Pennsylvania State University. The work was done by T. Furukawa under the supervision of Professor W. B. White. The melting history of glasses sent for the Raman spectroscopy are given in Table 9.

TABLE 5. EFFECT OF TIME AND TEMPERATURE ON THE REMOVAL OF RESIDUAL CARBON DURING THE MELTING OF GELS PREPARED BY PROCEDURE I

Experiment No.	Thermal Treatment Prior to Melting	Melting Temperature (C)	Melting Time (Hours)	Appearance
(1)	After Infrared Drying	1000	2	Grey Colors, Transparent Numerous Bubbles
(2)	After Infrared Drying	1000	3	Colorless and Transparent, Less Number Bubbles
(3)	After Infrared Drying	1000	4	Colorless and Transparent, much Less Bubbles
(4)	After Infrared Drying	1000	5	Highly Transparent, Bubble Undetected
(5)	After Infrared Drying	1100	2	Quite Transparent and Colorless, no Detectable Bubbles
(6)	After Infrared Drying	1100	3	Highly Transparent Colorless, no Bubbles
(7)	After Infrared Drying	1200	1	Transparent Colorless, no Bubbles
(8)	After Infrared Drying	1200	2	Transparent Colorless, no Bubbles
(9)	After Thermal Treatment up to 500 C	1000	5	Transparent Glass after 5 Hours
(10)	After Thermal Treatment up to 500 C	1100	3	Transparent Glass
(11)	After Thermal Treatment up to 500 C	1200	2	Transparent Glass

TABLE 6. EFFECT OF TIME AND TEMPERATURES ON THE REMOVAL OF RESIDUAL CARBON DURING THE MELTING OF GELS PREPARED BY PROCEDURE II

Experiment No.	Thermal Treatment Prior to Melting	Melting Temperature (C)	Melting Time (Hours)	Appearance
(1)	After Thermal Treatment at 500 C	1000	1	Transparent
(2)	After Thermal Treatment at 500 C	1000	2	Transparent
(3)	After Thermal Treatment at 500 C	1000	4	Transparent

TABLE 7. EFFECT OF TIME AND TEMPERATURE ON THE REMOVAL OF RESIDUAL CARBON DURING THE MELTING OF GELS PREPARED BY PROCEDURE III

Experiment No.	Thermal Treatment Prior to Melting	Melting Temperature (C)	Melting Time (Hours)	Appearance
(1)	After Thermal Treatment at 500 C	1000	1	Transparent with some Black Residue
(2)	After Thermal Treatment at 500 C	1000	2	Transparent with some Black Residue
(3)	After Thermal Treatment at 500 C	1000	4	Transparent
(4)	After Thermal Treatment at 500 C	1200	1	Transparent with some Residue
(5)	After Thermal Treatment at 500 C	1200	2	More Transparent
(6)	After Thermal Treatment at 500 C	1200	4	Transparent

TABLE 8. CHARACTERISTICS OF THE IR ABSORPTION BANDS DUE TO Si-O-Si STRETCHING OF DIFFERENT GLASSES

Gel Preparation Procedure	Melting Temperature (C)	Melting Time (Hours)	Position of Absorption Band due to Si-O-Si Stretching (ν cm^{-1})
I	1000	2	1000
I	1000	3	1000
I	1000	3	1000
I	1100	2	1000
I	1200	1	1000
I	1200	2	1000
I	1200	4	1020
I	1400	2	1080
III	1200	1	1020
III	1200	2	1040
III	1200	4	1040

TABLE 9. MELTING HISTORIES OF THE SAMPLES FOR THE RAMAN SPECTROSCOPIC STUDIES

Sample No.	Gel Preparation Procedures	Melting Temperature (C)	Melting Time (Hours)
1	I	1200	2
2	I	1200	4
3	II	1000	2
4	II	1000	6
5	II	1200	1
6	II	1200	3-1/2
7	Conventional Glass Batch	1000	2
8	Conventional Glass Batch	1200	6

Experimental Conditions and Results. The instrument used for the Raman spectroscopic studies was an Spex Model 1401. The excitation source was a 514.5 nm green line, 400-700 MW.

The results of the Raman spectroscopic studies can be summarized as follows:

- (1) All the glasses produce similar Raman spectra
 - A weak band at 1475 cm^{-1} ; B-O stretching
 - A strong band at 1090 cm^{-1} ; Si-O (nonbridging) stretching
 - A fairly sharp peak at 630 cm^{-1} ; may be due to some boroxy group or borosilicate group.
- (2) Samples 4 and 6 seem to have a slightly stronger 1090 cm^{-1} band compared to the others, which indicates more Si-O nonbridging bonds.
- (3) No bands due to H_2O or OH were detected
- (4) All the mixtures luminesce in the red region.

Treatment for the Removal of Hydroxyl Groups from the Gels

The following steps were taken for the removal of hydroxyl groups:

- (1) Baking in an oven
- (2) Passing dry O_2 through the porous gels at 280 C
- (3) Passing thionyl chloride (SOCl_2) vapor carried by dry oxygen through the porous gels at 280 C
- (4) Subsequent melting of the thionyl chloride treated gels.

Three experiments were performed using the gels prepared by Procedure I. The details of these experiments are as follows:

Experiment I

After the drying of the gel in an oven at 150 C for 60 hours the gel was placed in a tube furnace. Dry oxygen was passed through the furnace as the temperature was raised to 280 C. Then the dry oxygen was bubbled through thionyl chloride and was passed through the porous gel at

280 C for 6 hours. The gel was, then, transferred to a platinum crucible kept overnight at 600 C and was, then, raised to 1100 C in 3 hours and allowed to soak at that temperature for 5 hours. A liquid-liquid separation was observed during the pouring of the melt. There existed a very fluid liquid on top of a very viscous liquid. The top liquid hardened to a white opaque mass while the bottom liquid was unpourable.

Experiment 2

First, dry oxygen was passed through the gel powders at 280 C for 4 hours. The gel was then placed in a furnace at approximately 500 C overnight. The melting was, then, done at 1200 C for 5 hours. The glass obtained was clear and bubble free, no liquid-liquid separation was observed.

Experiment 3

In this experiment, the gel powders were treated for 3 hours with dry oxygen followed by 1 hour with thionyl chloride vapor carried by dry oxygen. Subsequently, the gel was held overnight at 500 C and was then melted at 1200 C. A clear bubble free glass was obtained. No phase separation was observed.

DISCUSSION

The important parameters that control the gelling process are as follows:

- Chemical nature of the reactants
- pH of the medium
- Concentration of water
- Temperature
- Concentration and nature of the solvents.

In a multicomponent oxide system having oxides of markedly different chemical nature, it is extremely difficult to change the parameters independently. The homogeneous incorporation of large concentrations of alkali ions which have the least tendency for polycondensation is a difficult task. Hence, three different sources of alkali oxides were chosen.

In Procedure I, the alkali oxide was introduced as sodium methylate which is soluble in alcohol and, thus, can be mixed intimately with other constituents [e.g., $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{B}(\text{OCH}_3)_3$, or H_3BO_3] and dissolved in (methanol) nonaqueous solvents. But because of the high reactivity of sodium methylate with water, only a small amount of water can be added before the addition of sodium methylate. Consequently, there are some difficulties in achieving the complete hydrolysis and subsequent removal of alkoxy groups during thermal treatment. However, this problem can be avoided by taking appropriate measures such as the addition of a water-alcohol mixture or exposing the gel to a humid atmosphere.

In Procedure II, because sodium nitrate is not soluble in alcohol, an aqueous solution of sodium nitrate was used as the source of Na_2O . If the amount of water added is sufficiently high, sodium nitrate remains dissolved in the alcohol-water mixture and a clear gel is obtained. Subsequently, some of the sodium ions are incorporated into the gel structure, but a portion of the sodium nitrate remains as sodium nitrate shown by the fact that the removal of water during the surface drying causes the precipitation of sodium nitrate, which is evident from the x-ray diffraction pattern. However, in this procedure an excess of water added before gelation is beneficial for the hydrolysis of the chemically bonded alkoxy groups and, thus, the removal of organics becomes more effective.

In Procedure III, the source of sodium oxide was an aqueous solution of sodium acetate. In this case, an excess of water could be incorporated before the addition of sodium acetate, but the addition of sodium acetate solution changes the pH of the solution and a rapid gelation occurs. However, the hydrolysis of sodium acetate takes place, and, then a noncrystalline gel is obtained. Even in the presence of excess water, the removal of organic groups from the gel prepared by this pro-

cedure during thermal treatment is not very effective. This conclusion is noted from the color as well as the carbon content of the fired gel. This may be due to the incorporation of a large amount of acetate groups in the form of sodium acetate.

The results of the surface area evaluations on the gels prepared by different procedures show that the surface areas of the gels are strongly dependent on the preparation procedures.

The surface areas of the gels at various temperatures of thermal treatment are also different. This difference in surface area is most likely due to the nature and extent of porosity in the gel particles. It is desirable to have open porosity so that the removal of hydroxyl groups can be effective during the chemical treatment of the gels with thionyl chloride.

The different time and temperatures required for the removal of carbon from the different gels might be explained in terms of the entrapping of the residual organics in the closed pores which in turn would depend on the nature of the porosity and the rate of closing of the pores during the firing and melting cycle. The results of the infrared and Raman spectroscopic studies of the glasses made from the different gels and having different melting histories (e.g., time and temperature of melting) indicate that the molecular structures of the glasses made from the gels prepared by different procedures and melted at lower temperatures (≤ 1000 C) are not identical. However, the melting at higher temperatures (1100-1200 C) appears to be sufficient to give an equilibrium melt for each gel. Studies on glasses melted at lower temperatures (e.g., 700-1000) may throw some light on the process of approaching an equilibrium melt.

CONCLUSIONS

The following conclusions can be drawn from the results of the present work:

- Gels in the soda-borosilicate system having a composition (wt. %) $\text{SO}_2:60$; $\text{B}_2\text{O}_3:15$; $\text{Na}_2\text{O}:25$, can be prepared by three different procedures using three different sources of Na_2O .
- Gels produced by Procedure I and Procedure III are noncrystalline, and remain so after thermal treatment at 600 C for 40 hours, whereas the gel prepared by Procedure II using NaNO_3 are crystalline, due to the presence of residual sodium nitrate.
- The removal of organic groups during the thermal treatment below 500 C is related to gel preparation procedures, ambient atmosphere such as humidity and oxygen potential, and the rate of heating. The carbon content of the fired gel can vary from 0.1 percent to 0.6 percent by weight depending on the preparation procedure.
- The rate of removal of carbon from the glass during the melting depends on the gel preparation procedures and thermal treatment before melting. The removal of carbon from the gel prepared by Procedure II is most rapid, whereas the removal is most sluggish with the gel prepared by Procedure III.
- The rates of removal of carbon and the bubbles were also a function of temperature and time of melting in an air atmosphere.
- Molecular structures of the glasses melted at lower temperatures (≤ 1000 C) are not identical, however, the melting at higher temperatures 1100-1200 C appears to give an equilibrium melt from the different gels.

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