NON-SILICATE POROUS GLASSES OBTAINED BY THE LEACHING OF BORATE-RICH GLASSES

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ABSTRACT

Glasses of the composition Na_2O-B_2O_3-X-Y and Na_2O-B_2O_3-Al_2O_3-X-Y were made where X and Y are two of the oxides CeO_2, HfO_2, ThO_2, Y_2O_3, ZrO_2 or Ga_2O_3. The glasses were either quenched or heat treated to promote phase separation and/or crystallization. The materials were subsequently leached in distilled water for periods of up to 96 hours. Leaching resulted in porous glasses or porous crystalline materials.

The porous materials had high surface areas and good alkali resistance. A wide variety of compositions of these porous materials had BET surface areas between 100 and 413 m^2/g. Selected porous glasses were chemically analysed. The heat resistances of two porous glasses were evaluated by observing the temperatures necessary for densification. Electron micrographs and X-ray diffraction scans were taken where necessary.

Part of the glass forming regions for quenched samples of the system Na_2O-B_2O_3-Ga_2O_3-Y_2O_3 having Ga_2O_3 : Y_2O_3 ratios of either 3 : 1 or 3 : 2 were investigated. Part of the glass forming region for quenched samples of the Na_2O-B_2O_3-Y_2O_3 system was also investigated.

CHAPTER 1: INTRODUCTION

Porous glass with a silica content of about 96 per cent can be made by the Vycor process. In this process sodium borosilicate glasses within a certain compositional range are heat treated so that they separate into two non-crystalline phases. The borate-rich phase is then leached out with acid or water leaving a silica-rich porous glass. This porous glass may be densified to a clear non-porous glass when it is heated to about 1 000 °C. Applications exist for both the porous and the densified product. For example, due to the controllable pore size, the porous glass may be used as a column packing material for steric exclusion chromatography. Disadvantages of this porous high-silica glass includes a low alkali resistance (this is a disadvantage for certain applications, for example, in the desalination of alkaline waters) and a relatively low working temperature (so that densification does not occur). The non-porous high-silica product may be used for high temperature laboratory ware. It is resistant to attack by many acids, neutral solutions, gases and molten metals. Besides their applications, the phase-separable glasses are used in studies of the glassy state.

At the Council for Scientific and Industrial Research (CSIR), Pretoria studies were carried out by Res and co-workers with the aim of improving upon the alkali resistance and heat resistance of the porous high-silica materials. Melts were prepared where SiO_2 in the system Na_2O-B_2O_3-SiO_2 was substituted totally by one or more other oxides. It was noted that systems containing one or more of these "silica replacing" oxides showed

regions of glass formation over a composition range which normally contained a high B_2O_3 content. Unpublished work by Res and co-workers showed that for oxides such as Ga_2O_3, CeO_2, La_2O_3 and Ta_2O_5 the region of glass formation appears to be more extensive than for other oxides such as ZrO_2, Al_2O_3 and TiO_2. When selecting the "silica replacing" oxides preference was given to oxides having a high alkali and/or heat resistance.

If oxides having a high melting point and good alkali resistance are used a glass having an improved heat resistance and alkali resistance after leaching may be expected. Melts of these non-silicate materials were processed by a method similar to that used for preparing Vycor glass. An outline of the processes followed for making the porous glass or thermally densified materials is depicted in Figure 1. After melting the glasses they were either quenched by pouring onto a steel plate at room temperature or annealed. Annealing was done by casting the melt into an iron mould heated to a predetermined temperature and allowing the sample to furnace anneal to room temperature.

For this investigation glasses were selected where SiO_2 in the Na_2O-B_2O_3-SiO_2 glass system was replaced by a combination of two heat and/or alkali resistant oxides. The usual processes detailed in the flow chart of Figure 1 were carried out. The glasses were leached to give a porous material having a lower B_2O_3 and Na_2O content than the original unleached glass. For certain porous (leached) glasses an attempt was made to densify the glass to obtain a non-porous material. Physical and chemical properties were investigated at the relevant stages of the process.

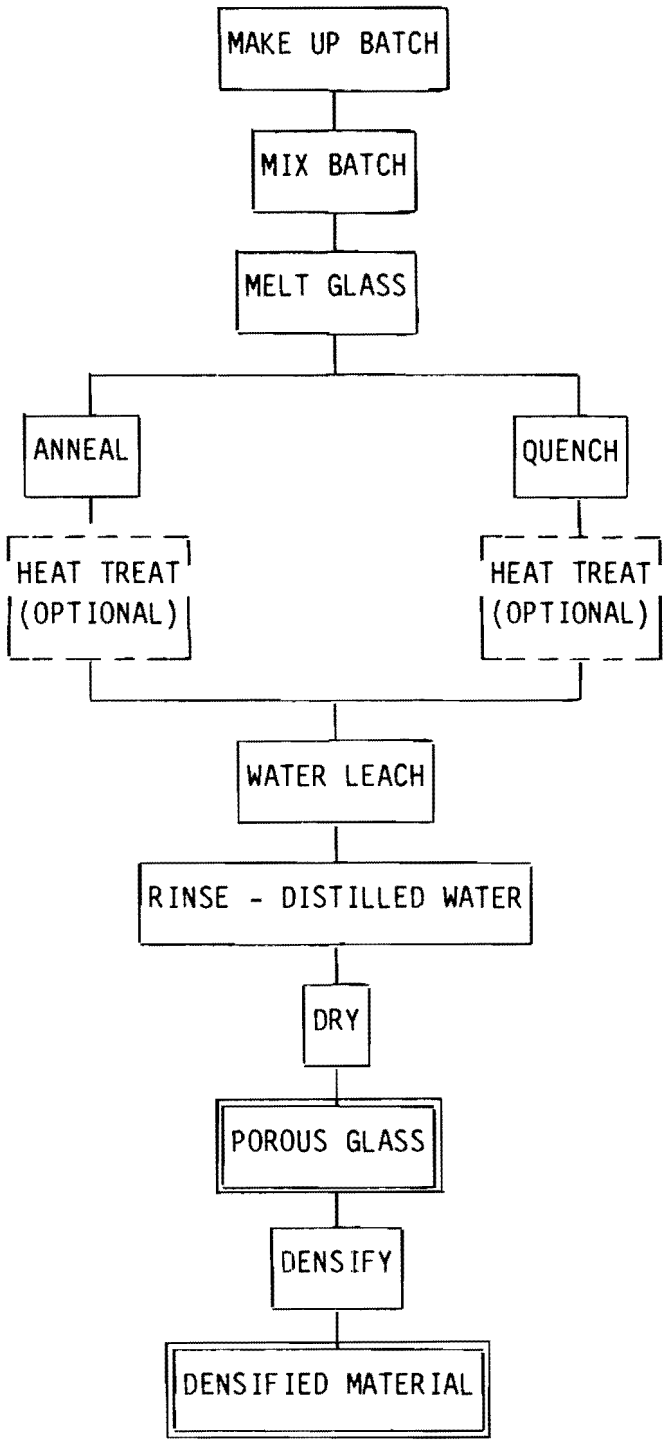


FIGURE 1: A flow sheet showing the overall process for making the porous or densified product.

It should be pointed out that the object of this work was to leach selected samples and to measure certain of their properties. It was expected that after leaching, glasses and partially crystalline materials of high surface areas, good alkali resistance and reasonable heat resistance could be obtained. The aim was also to broaden the knowledge of the glassy state since only a limited amount of work appears to have been done on glasses having similar compositions to those studied. The object was not to directly study the effect of changes in composition and heat treatment upon the properties of these materials, which would have required a different approach.

The subject matter of this thesis is divided into two parts.

Initially sodium borate glasses were made at the CSIR and these glasses contained two of the following five oxides: CeO_2, HfO_2, ThO_2, Y_2O_3 and ZrO_2. The leachability of these materials in hot water and their surface areas were evaluated. Based on information from these glasses further glasses were made with similar compositions which, after leaching, were expected to give high surface areas and good alkali resistance. The two glasses concentrated on most contained ZrO_2-Y_2O_3 in the one case and CeO_2-HfO_2 in the other, in addition to the usual Na_2O and B_2O_3. This work forms the first part of this thesis and these glasses are termed Series 1 glasses which are subdivided into Series 1(A), 1(B) and 1(C) glasses.

As a result of previous work carried out by Res et al. (1984) the system Na_2O-B_2O_3-Ga_2O_3 was known to have an extensive glass forming region. Results from the Series 1 glasses as well

as other results obtained at the CSIR from unpublished work by Res, have shown that leached glasses containing Y_2O_3 often have a high surface area. These two factors helped provide the incentive to investigate samples from the Na_2O-B_2O_3-Ga_2O_3-Y_2O_3 system which are called Series 2 glasses and are subdivided into Series 2(A) and 2(B) glasses.

CHAPTER 2: LITERATURE REVIEW

2.1 PHASE SEPARATION IN GLASSES

Phase separation occurs over substantial regions of composition in all the alkali borates, all the alkaline earth borates and in many other binary glass systems. Phase separation has also been reported in many ternary systems including the Na_2O-B_2O_3-SiO_2 system.

There is not yet a generally accepted understanding of the molecular interactions which are decisive in the occurrence of miscibility gaps. A number of models have been advanced to theoretically predict immiscibility boundaries in glass systems. One approach is to use thermodynamic principles.

The free energy of mixing can be expressed in terms of the enthalpy and entropy of mixing. If the enthalpy is positive then phase separation may occur. One method of obtaining the free energy of mixing is to use the regular solution model. The basic derivation of regular mixing equations for a binary system was reviewed by Macedo and Simmons. Miscibility gap boundaries are obtained by minimising the free energy of mixing, ΔG_m, with respect to composition, that is

$$\frac{\partial \Delta G_m}{\partial y} = 0$$

The spinodal curve is calculated by letting the second derivative of ΔG_m with respect to composition go to zero, that is

$$\frac{\partial^2 \Delta G_m}{\partial y^2} = 0$$

This is because within the spinodal region small variations in composition result in a lower free-energy for the system. Therefore the compositions corresponding to the points of inflection on the free-energy versus composition curves lie on the spinodal curve within the miscibility gap.

Macedo and Simmons used an approach based on the regular solution concept to describe immiscibility in alkali borate binary systems. It is assumed that the mixing occurs between the network former and a stoichiometric chemical compound whose composition can be obtained by extrapolating the experimentally obtained immiscibility curve to zero Kelvin. In the lithium borate system, for example the two demixing liquids were considered to be $(B_2O_3)_5$ and $Li_2O{\cdot}4B_2O_3$. Such a regular solution equation fitted observed miscibility gaps of five different borate binary systems reasonably well. But the authors point out that the assumption of the existence of complex glass-former structures in the melt, for example $(B_2O_3)_5$, has not been independently confirmed but does account for the behaviour of a number of physical properties of molten oxide glasses.

As far as predicting the immiscibility boundaries of ternary glass systems is concerned Kawamoto and Tomazawa have developed a method for ternary silicate glasses if the immiscibility boundaries of the two relevant binary silicates are known. The method

is based upon the similarity in shape of the immiscibility boundaries of silicate systems and the use of the regular mixing equation.

Tomozawa has reviewed the morphology and kinetics of phase separation in glasses. There are theoretically two mechanisms by which a homogeneous glass may transform into a two-phase structure (Figure 2). One is the nucleation and growth mechanism which is expected to operate in the metastable region between the immiscibility boundary and the spinodal line, that is where

$$\frac{\partial^2 \Delta G_m}{\partial y^2} > 0.$$

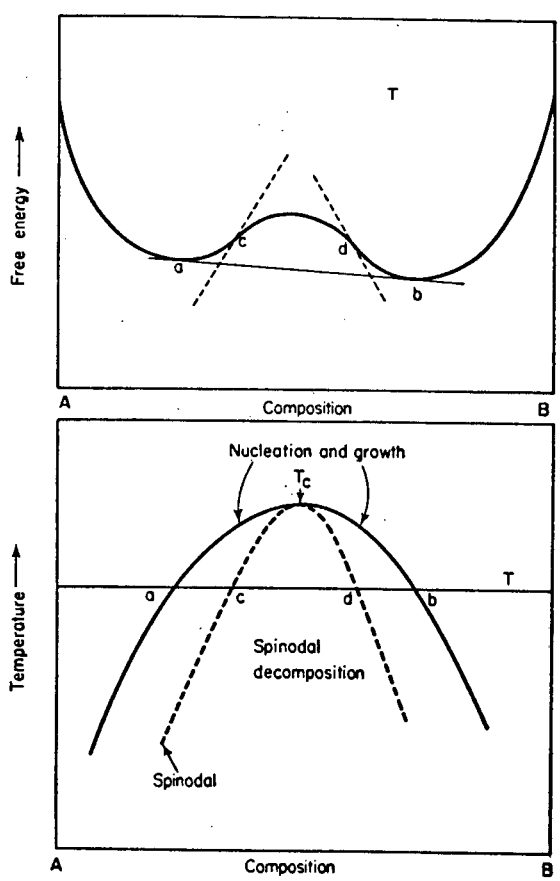


FIGURE 2: Free energy-composition and phase diagram illustrating the regions in which different types of phase separation may occur (reproduced from Rawson).

Spinodal decomposition is expected in the unstable region inside the spinodal line, in other words where

$$\frac{\partial^2 \Delta G_m}{\partial y^2} < 0.$$

According to Uhlmann and Kolbeck, whether the initial phase separation occurs by nucleation and growth or by spinodal decomposition, the scale of the resulting microstructure is usually sufficiently small for the free energy of the system to be substantially reduced by a coarsening process. The driving force for coarsening is a reduction in total interfacial area between the phases. Analyses of diffusion controlled coarsening for discrete second phase particles indicate that the dimensions of the particles increase as a function of $(\text{time})^{1/3}$. Provided the volume fractions are constant during coarsening, the number of particles should decrease as a function of $(\text{time})^{-1}$. Diffusion controlled coarsening of interconnected structures has also been analysed to various degrees of approximation. The results again indicate that the linear size increases as a function of $(\text{time})^{1/3}$. The temperature dependence of the growth rate follows an Arrhenian relationship, that is to say, volume growth rate $V = B \exp\left(\frac{-E}{RT}\right)$ where E is the activation energy for the process and B is a constant.

Experiments by Takamori and Tomazawa provided evidence that during heat treatment the composition of the two phases is continuously changing, as is expected during spinodal decomposition. Commercial borosilicate glass specimens were heat treated

for different periods of time to cause phase separation. For a number of different temperatures increased heat treatment time resulted in an increase in HCl leaching rate and an increase in viscosity. The chemical durability, measured as the HCl leaching rate, was thought to be primarily determined by the composition of the alkali-borate-rich phase.

Vogel gives examples of glasses where three or more phases have been detected. For example, after phase separation by stages, six microphases were visible in a replica electron micrograph of a barium borosilicate glass. During a multi-stage phase separation process a primary separation process occurs first. During cooling of the two phases each behaves almost as a separate system with a separation process of its own.

The borosilicate glasses used for making Vycor are by far the most well documented phase-separable and leachable glasses. The glasses investigated in this work have compositional and other similarities to Vycor glasses and therefore comparisons with Vycor glasses are made. The term Vycor-type glass has been loosely used in this work and is meant to refer to a glass which has been produced by a process which is similar to the process for making Vycor glass.

2.2 VYCOR GLASSES

2.2.1 Starting compositions which yield leachable glasses

Volf gave a history of the development of Vycor glasses. The original glasses used in the manufacture of Vycor belong to the alkali borosilicate glasses, R_2O-B_2O_3-SiO_2, where R_2O may be Na_2O, K_2O or Li_2O. The alkali metal oxide behaves as a flux to

reduce the melting temperature of the glass. In their patent Hood and Nordberg (1938) reported on a range of compositions for the three alkali borosilicate systems where the alkali oxide is Na_2O, K_2O or Li_2O. These glasses could all be phase separated and leached to yield a porous silica-rich skeleton. Figure 3 shows a region of the Na_2O-B_2O_3-SiO_2 system for producing Vycor glasses. A composition of less than 60 per cent silica for the starting glass will yield a structure which is mechanically weaker after leaching and these regions of the system are not covered by this patent. It is reported that inside the X region phase separation proceeds very rapidly, so that it occurs already during the shaping and cooling of the article, while in the Y region phase separation only takes place during the subsequent heat treatment.

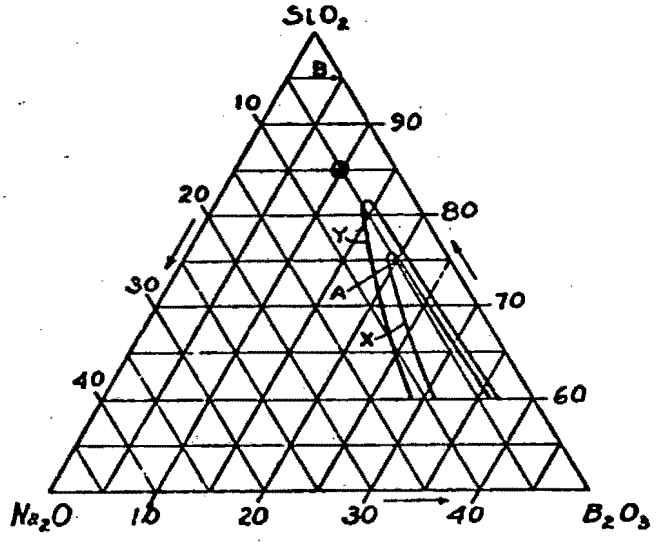


FIGURE 3: Part of the region of leachable and sinterable glasses for the Na_2O-B_2O_3-SiO_2 system (after Hood and Nordberg, 1938).

During acid leaching of glasses a swelling or shrinking of the glass occurs. Such swelling or shrinking establishes strains in the glass which may cause fracture. Cracking during leaching may be controlled through proper adjustment of the original composition, heat treatment and leaching conditions. Hood and Nordberg (1940) found that by a convenient selection of the composition of the glass and an adequate procedure during phase separation this strain may be reduced to a minimum. They developed glasses with a silica content of 55 to 70 per cent by weight having minimum stresses which are said to lie on what they termed the optimum line given by the formula:

SiO_2	55 to 70 per cent by weight
Na_2O	10 to 0,1 (SiO_2 - 55) per cent
B_2O_3	balance up to 100 per cent.

Hood and Nordberg (1940) also patented glasses with a starting composition containing up to 4 per cent Al_2O_3. A small amount of the Al_2O_3 is retained in the insoluble silica -rich phase producing a Vycor glass which is more stable against devitrification after sintering.

Hammel and Allersma described a method where a lower SiO_2 content was used in the starting composition to produce a porous glass having a higher pore volume. The high pore volume and good thermal stability made this porous glass suitable as a catalyst support. The starting composition, which is $9,4Na_2O$ - $49,6B_2O_3$ - $41,0SiO_2$ (by weight), is melted and formed into glass beads. The beads are oil quenched and heat treated at 480 °C for 4 hours. The temperature is reduced from 480 °C to room temperature over a further period of about 5 hours. Water leaching is

carried out at 95 °C for 8 hours followed by rinsing in deionised water for 4 hours. Acid leaching is now carried out in 0,3N HNO_3 solution for 6 hours followed by a final rinse in deionised water for 4 hours. The beads are air dried at 85 °C.

The beads are claimed to have a 98,6 per cent silica content. Preshrinking may be carried out to increase dimensional stability at elevated temperatures and mechanical strength. Preshrinking at 980 °C for 24 hours reduced the surface area by 43 per cent and the pore volume by 26 per cent.

The glasses studied in this work also have a starting composition with a high Na_2O plus B_2O_3 content. High pore volumes can therefore be expected after leaching.

2.2.2 Heat treatment

The best heat treatment to cause phase separation should result in a continuous soluble phase and not a discrete droplet-like soluble phase. This is desirable for optimum leaching results. The heat treatment temperatures are below the immiscibility temperature but because phase separation requires diffusion the heat treatment temperatures are above the glass transition temperature for kinetic reasons. Optimal temperatures and time for heat treatments have been experimentally determined. Heat treatment is usually carried out between about 480 °C and 600 °C. For example, Hood and Nordberg (1938) stated that for a glass with a composition $75SiO_2$ - $5Na_2O$ - $20B_2O_3$ by weight a heat treatment at 525 °C requires three days whereas a heat treatment at 600 °C takes a few hours for adequate phase separation.

According to Volf the tendency to separate into two phases is considerably weakened by the action of Al_2O_3, while it is, on the other hand, promoted by elements possessing a marked polarizing ability, for example W or Zr.

The silica-rich phase formed by phase separation in sodium borosilicate glasses has a lower thermal expansion value than the borate-rich phase. It is therefore impossible to obtain completely strain-free Vycor glasses after heat treatment. Hammel and Allersma state that the presence of Na_2O in their patented sodium borosilicate glass reduces the difference in thermal expansion between the two phases. This is partly due to Na_2O in the borate-rich phase which has the effect of reducing the thermal expansion of that phase because of the boron anomaly.

2.2.3 Leaching

Leaching is generally carried out in HCl, H_2SO_4 or HNO_3 having a concentration of between 0,1 N and 3 N.

Volf explains that during leaching a strain may be induced either by the swelling of the leached layer, or alternatively, by the shrinking of the leached layer. Glasses with compositions lying to the left of the optimum line (i.e. more Na_2O) shrink while those lying to the right (i.e. less Na_2O) develop stress through swelling. Shrinking involves a greater risk than swelling because it sets up dangerous tensile stresses in the brittle and weak leached layer. It is said that swelling of the leached layer can be reduced by saturating the leaching bath with ammonium chloride or adding 20 per cent of potassium

chloride. According to Hood and Nordberg (1938) this may be explained by assuming that the concentration of water in the acid solution has been reduced, which in turn reduces the amount of water adsorbed by the silica structure and the swelling caused thereby.

Leaching is a slow process and according to Hood and Nordberg (1938), about 24 hours in an acid bath at 93 °C is required to leach through 1 mm of wall-thickness for an article containing about 60 to 80 per cent silica by weight. In other words, an article which is 2 mm thick will require about 2 days immersion for complete penetration of the acid. According to Volf small amounts of aluminium, sodium and boric oxides remain in the porous silica glass after leaching. Divalent and trivalent elements (Pb, Fe, Co) tend to concentrate in the soluble phase and are leached out with it.

One gram of porous Vycor glass has about 120 to 200 m^2 of internal surface area.

2.2.4 Sintering

After drying Vycor can be sintered (densified) at temperatures of between 900 and 1 200 °C and the glass becomes non-porous and transparent. The coefficient of thermal expansion (α_{20-300}) of Vycor, as given by Volf, is about 8×10^{-7} $°C^{-1}$. The corresponding value for pure silica glass is given as $5{,}5 \times 10^{-7}$ $°C^{-1}$.

2.3 VYCOR-TYPE GLASSES

Since the discovery of Vycor glasses work has been carried out to replace, partly or totally, the oxides in the ternary

system Na_2O-B_2O_3-SiO_2 to develop porous glasses having different properties.

Haller reported that Na_2O could be substituted to a greater or lesser extent by CaO, BaO, MgO, BeO, SrO_2, ZnO_2 or PbO_2 or a combination thereof. Haller also reported that SiO_2 could be totally substituted by GeO_2.

Plank and Woodbury described a process for preparing borosilicate glass containing Al_2O_3 and P_2O_5 which is suitable for converting into a porous glass. The glass has a composition in weight per cent within the following limits: 3 to 10 Na_2O, 15 to 45 B_2O_3, 25 to 70 SiO_2, 5 to 15 Al_2O_3 and 7 to 24 P_2O_5. Preferably the melt should contain an amount of P_2O_5 approximately equivalent to the Al_2O_3 on a molar basis and therefore these oxides may be added in the form of $AlPO_4$. After heat treating, the glass may be leached in hot water which results in a porous glass. In many cases, with no heat treatment other than that necessary for annealing the glass, it may be leached with water to form a porous glass.It is claimed the porous glass consists essentially of SiO_2 with some Al_2O_3 and minor amounts of other oxides. Leaching in water at 90 to 100 °C is relatively rapid, taking about 8 hours to complete if the glass is about 2 to 3 mm thick.

Rabinovich et al. reported on some glasses of the Na_2O-P_2O_5-SiO_2 system. Melts poured on a cold steel plate cooled to either transparent, opalescent or crystalline material. X-ray diffraction examination of some of the opalescent glasses failed to detect a crystalline phase, so that this opalescence could be attributed to liquid immiscibility. Glasses were

heat-treated to induce or enhance phase separation. In some cases partial crystallization resulted. Scanning electron microscope studies of phase separated glasses showed both interconnected and droplet phases. Droplet phases were observed after heat-treating at higher temperatures (compared to the heat treatment temperatures causing interconnected morphologies) and these specimens also disintegrated during leaching. Specimens were leached in 3N HCl at 50 °C and rinsed in distilled water. Leaching out the high phosphate phase resulted in a high-silica (over 90 per cent SiO_2) skeleton, which could be densified at 900 to 1 100 °C.

According to Makishima et al the leaching rates of phase-separated borosilicate glasses can be increased by the addition of a fourth oxide. The base glass composition used was $10Na_2O$ - $50B_2O_3$ - $40SiO_2$ by weight per cent. Melts were also made where from 1 to 10 per cent of V_2O_5, P_2O_5, WO_3 or MoO_3 was added to the base glass composition. The glasses were heat-treated at 550 °C for 2 hours to cause phase separation and leaching was done in water at 90 °C. It was assumed that the borosilicate glass separated into an insoluble phase (nearly 100 per cent SiO_2) and a soluble borate phase containing the fourth oxide. Glass containing 5 per cent P_2O_5 had a leaching rate about four times faster than the original base glass composition and about twice that of the V_2O_5 containing glass. MoO_3 and WO_3 also increased the leaching rate of the base glass. The solubility of bulk sodium borate glass (of the estimated phase-separated composition) was experimentally found to be less than that of the same borate glass containing V_2O_5, P_2O_5, MoO_3 or WO_3. This helps explain why the added oxide increases the leaching rate in the sodium borosilicate glass. The results indicated that

the presence of these oxides in the soluble phase can suppress the boron anomaly. The boron anomaly is a result of the formation of BO_4 tetrahedra when alkali oxides are added to B_2O_3. This effect would then allow for part of the borate glass structure to exist in the form of pure boron oxide glass which has a higher solubility in water than sodium borate glass.

Vogel notes that many binary borate and silicate melts exhibit phase separation. For instance, binary borate and silicate glasses containing elements of the third group of the Periodic Table (Al, Ga, Tl, Y, La) tend to segregate, their systems having miscibility gaps. Also binary borate and silicate glasses containing elements of the fourth group (Sn, Pb, Ti, Zr, Hf, Th) have a strongly marked trend towards microphase separation. The fact that B_2O_3-SiO_2 melts, mixed in any proportion appear homogeneous to the eye is due to the fact that phase separation zones in such glasses are extremely small, so that they escaped detection until instruments such as the electron microscope were used to examine the microstructure. Electron microscopy, which has to be credited for initiating the advancement of glass structure analysis, was later complemented, and its results confirmed, by refined methods of small-angle X-ray scattering and also light scattering.

The Morey-Eastman Kodak Glasses were discussed briefly by Weyl and Marboe. These glasses have compositions containing a low proportion of conventional glass-formers. They are based on mixtures of oxides such as TiO_2, Ta_2O_3, La_2O_3, ZrO_2 and ThO_2, compounds which do not form glass by themselves. Some of the compositions contained the glass-former B_2O_3 in the order of about 10 to 20 per cent by weight. This group of glasses,

although quite different from Vycor glasses, is mentioned because they have a composition that is comparable to some of the porous glasses made by Res and co-workers (for example Res (1983)). These porous glasses also contain of a low proportion of conventional glassformers, with B_2O_3 being present as a minor constituent.

Work has been carried out by Res and co-workers on the replacement of SiO_2 in the sodium borosilicate system by oxides of Ce, Nb, La, Ta, Al and other elements. Res et al. (1982) reported that Na_2O-B_2O_3-CeO_2-Nb_2O_5 glasses showed phase separation, leachability and subsequent porosity. Similar results were reported by Res et al. (1983) where again high melting point oxides were substituted for SiO_2. These oxides were CeO_2, ZrO_2, Y_2O_3, ThO_2, HfO_2 and La_2O_3. Various combinations of these oxides were used in some glass melts while for other samples all six were used. After heat treatment the sodium borate-rich phase was leached out in boiling distilled water. This resulted in a porous material which could be either glassy or partially crystalline. Surface areas of these materials were up to about 300 m^2/g, which is comparable to values for silica-based porous glasses. The high temperature resistance of some of these materials is demonstrated by the temperature of about 1 500 °C required for sintering. For comparison the sintering temperatures of porous silica (according to Volf) are between 900 ° and 1 200 °C. For certain samples electron micrographs confirmed the suspected microphase separation. Res et al. (1984) reported that a series of Na_2O-B_2O_3-Ga_2O_3 melts showed phase separation, leachability and subsequent porosity similar to that achieved in the ternary sodium borosilicate system. Phase separation and/or crystallization was present in

heat-treated samples. For example, a glass having a batch composition of 10,5 Na_2O - 54,5 B_2O_3 - 35,0 Ga_2O_3 by weight was heat treated at 550 °C for 24 hours and leached in boiling distilled water to give a porous product. An X-ray diffraction pattern of this porous material showed a well defined spectrum identified as monoclinic β-Ga_2O_3. Another sample was heat treated and chemically analysed before and after leaching in hot water. The composition was analysed as 7,6 Na_2O - 48,1 B_2O_3 - 43,8 Ga_2O_3 by weight per cent before leaching. After leaching the resulting glass was found to contain 93,5 per cent Ga_2O_3, the balance being B_2O_3, which showed that it was possible to leach out nearly all the Na_2O and most of the B_2O_3.

CHAPTER 3: EXPERIMENTAL AND ANALYTICAL TECHNIQUES

3.1 GLASS PREPARATION

The glasses were prepared from reagent grade H_3BO_3, Na_2CO_3 and the metal oxides which are listed under individual glass compositions.

The melts were carried out in either Pt/Rh or alumina crucibles in an electrically heated furnace with SiC elements and in an air atmosphere. Melting temperatures were 1 400 to 1 480 °C for 4 hours. Samples were quenched by pouring onto a cold steel plate. When annealed samples were also required a portion of the melt was cast into an iron mould heated to a predetermined temperature which was either 520, 550 or 600 °C and allowed to furnace anneal to room temperature. The furnace temperature during annealing decreased from 600 to 200 °C over a period of 4 hours and from 550 to 200 °C over a period of 3 hours 40 minutes.

3.2 HEAT TREATMENT

The aim of the heat treatment process was to obtain a material with a soluble phase that could be leached out within as short a time as possible.

Heat treatment was carried out empirically in steps of progressively higher temperatures (usually 50 °C steps for 2 or 3 hours at each temperature). The stepwise heat treatment was used to try to induce or enhance a phase-separated structure rapidly without deforming the samples. A relatively low starting temperature such as 550 °C was chosen. After each step of heat treatment

the sample was checked for a change to an opalescent, translucent or opaque appearance which would indicate that phase separation or crystallization had taken place. When this occurred the heat treatment was stopped. Afterwards a larger quantity of samples may be heat treated leaving out one or more of the initial steps at lower temperatures where the rate of phase separation is low. Softening and rounding of the edges of the glass specimen is taken as an indication that the heat treatment temperature is too high. In the case where phase separation had been successfully achieved in a sample then other samples of similar composition were normally found to respond to the same or a similar heat treatment. For certain glasses where the transformation temperature (Tg) of the glass was determined using the dilatometer the Tg was useful as a lower limit for the heat treatment temperature. For example, where the heat treatment is listed as 550/3 + 600/3 this means that the sample was heated to 550 °C, soaked for 3 hours, then the temperature was increased to 600 °C and kept there for a further 3 hours before removal. The rate of temperature increase between temperature steps was about 4 °C per minute.

3.3 LEACHING

To prepare samples for leaching, quenched samples were broken into irregular shapes by a hammer and annealed samples were cut into rectangular shapes. Batches of samples for leaching weighed between 1 and 12 grams with a maximum thickness of 4 mm, the actual thickness depending on the expected leaching rate. Leaching was carried out in boiling distilled water for times of between 24 and 96 hours. Figure 4 shows a diagram of

the leaching apparatus. After the leaching time had expired the leaching solution was poured out and replaced by distilled water and boiled for a further 1 hour to rinse the sample.

3.4 WEIGHT LOSS DUE TO LEACHING

As a control of the leaching process weight loss measurements were made. They show the difference in weight of the sample before and after leaching. To obtain the weight after leaching the leached samples were dried in an oven at 130 °C for at least 2 hours before weighing.

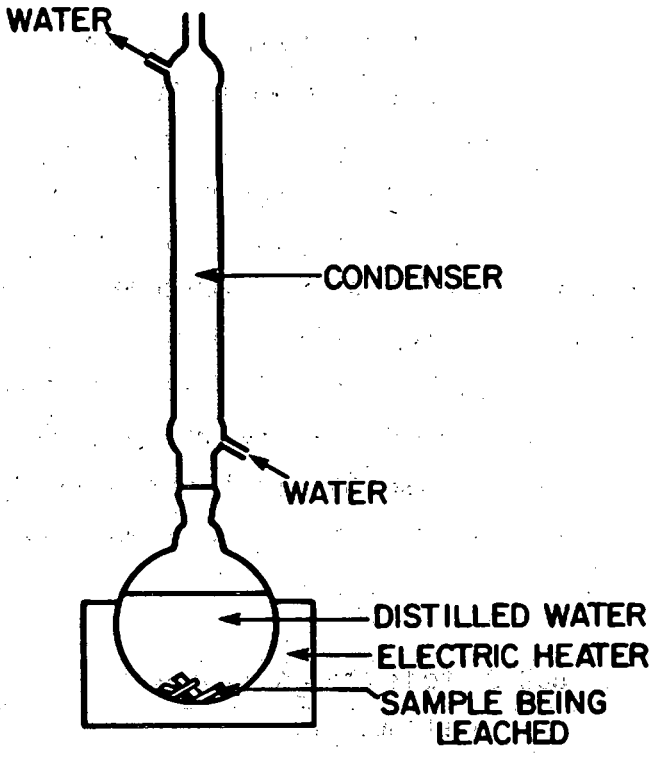


FIGURE 4: Schematic diagram of the leaching apparatus

3.5 LEACHING RATE

This was the estimated leaching rate which was useful as a guide to determine the number of days which a sample should be leached in cases where leaching was to be repeated. For example if a sample was measured by vernier as 2 mm thick and was completely leached through after 4 days the leaching rate was given as 0,5 mm/day although 4 days is not necessarily the minimum time required to completely leach the sample. Previous results of de Villiers showed that the leaching rate of a phase-separated glass having a sodium borate content of 49,1 per cent was approximately constant. The glasses leached in this work are assumed to have an approximately constant leaching rate.

3.6 DETERMINATION OF SURFACE AREA

Only completely leached (porous) portions of the sample were used when measuring the surface area. To prepare the sample for surface area measurement the sample was placed in a 130 °C oven to expel adsorbed gas. The weight of nitrogen adsorbed by the sample at 200 mm pressure at a temperature close to the boiling point of nitrogen was measured. The well-known equation derived by Brunauer, Emmett and Teller (BET equation) for multilayer adsorption was applied to estimate the surface area. A further commonly applied approximation was used whereby it is assumed the BET plot passes through the intercept so that a single point determination may be made. The BET surface area was calculated as follows:

$$\text{Surface area } (m^2/g) = \frac{(2{,}41 \times \text{mg } N_2 \text{ adsorbed at 200 mm pressure})}{\text{wt. sample (grams)}}$$

with 2,41 = constant from the BET equation.

3.7 DETERMINATION OF VOID VOLUME

A sample of the porous material was placed in a drying oven at 130 °C for at least 2 hours, cooled in a desiccator and then weighed. The sample was then totally immersed in distilled water. When bubbles stopped emanating from the sample it was transferred to an apparatus containing a relative humidity detector to measure evaporation rate. Evaporation rate is traced by a recorder. When the evaporation rate decreased due to pore moisture evaporation being slower than the outer surface evaporation rate, the sample was removed and reweighed.

$$\text{Void volume (m}\ell\text{/g)} = \frac{\text{weight increase due to water content (gram)}}{\text{weight of dry sample (gram)}}$$

The density of water is not taken into account as this error is negligible compared to other errors. Void volume measurements could not be taken for weak, brittle samples which disintegrated into small particles because of the experimental difficulties encountered during the handling of this type of material.

3.8 ALKALI RESISTANCE

The method used to measure alkali resistance was based in general on ISO 695, a standard method for determining alkali resistance of glass. Deviations from ISO 695 were made as this was thought to be desirable due to the porous nature of the material.

To measure the alkali resistance 0,3 to 0,5 g of leached sample was dried by placing in a 130 °C oven for 2 hours and then weighed. This sample was boiled in a mixture of 75 mℓ 1N NaOH and 75 mℓ 1N Na_2CO_3 for 3 hours. Afterwards it was rinsed in boiling distilled water for 15 minutes.

The sample was then dried at 130 °C for 2 hours and reweighed to obtain the weight loss.

$$\text{Alkali resistance } (mg/dm^2) = \frac{\text{weight loss (milligrams)}}{\text{surface area } (dm^2)}$$

The surface area is the BET surface area of the sample determined prior to boiling in the alkali mixture.

3.9 CHEMICAL ANALYSIS OF LEACHED SAMPLES

The analytical method used to determine the concentration of elements Na, B, Zr, Y and Ga in the sample was inductively coupled plasma atomic emission spectroscopy (ICPAES). The leached sample was dried and then dissolved in a 3,6 per cent HCl solution. The standard solutions were also made in 3,6 per cent HCl.

3.10 X-RAY DIFFRACTION

Powder X-ray diffraction with CuK_α radiation was used to either confirm a glassy state or identify any crystalline phase which may be present. The X-ray diffraction system used was either a Rigaku D_{max} III instrument or a Philips type PW2213/20 instrument.

3.11 SINTERING

The purpose of sintering was to follow structural changes and to establish the temperature/time requirements for densification of the material. An electrically heated furnace was heated to the desired sintering temperature. The leached glass to be

sintered was placed on a graphite block and then inserted into the furnace for 5 minutes.

3.12 DETERMINATION OF BULK DENSITY

The samples were placed in water to check whether bubbling occurred due to open porosity. If there was no bubbling Archimedes method was used to determine the bulk density. Due to the brittle nature of the samples the bulk densities of glasses having open porosity was estimated by the following method:

The sample was crushed and sieved to collect particles which passed through a 1 mm sieve but were retained by a 0,5 mm sieve. The particles were poured into a small container of 0,5 cm^3 made by drilling a cavity in a perspex block. Excess particles were carefully scraped off with a flat edge of paper so that the 0,5 cm^3 volume was just filled. The container with the particles was weighed so that the weight of particles occupying 0,5 cm^3 could be obtained.

Bulk density (g/cm^3) = weight of 0,5 cm^3 particles (grams) x 4

The constant 4 used in the above formula comes from 2 sources, a) to convert 0,5 cm^3 to 1 cm^3 and b) to correct for the air spaces between particles which occupied close to 50 per cent of the 0,5 cm^3 cavity. The air space was estimated by weighing the container with particles of a known bulk density and similar particle size distribution.

3.13 PREPARATION FOR SCANNING ELECTRON MICROSCOPE

For fracture surfaces of leached or unleached samples no preparation was done besides the Au-Pd coating. To obtain a polished and etched surface the specimen was first mounted in a thermoplastic resin. Using water as a lubricant the specimen was then ground on SiC grinding discs of progressively finer grit size ending with a 1200 grit size disc. Polishing was done with alpha alumina optical finishing powder of 17,5, 9,5, 3,0 and then finally 0,3 micron particle size. Water was used as a lubricant. The polished specimens were etched with distilled water for times of between 10 and 60 seconds. The specimens were then cleaned ultrasonically in ethanol. A Au-Pd coating for the electron microscope was given for 4 minutes at 2,5 kilovolts.

3.14 THERMAL EXPANSION

A Leitz light spot dilatometer was used to obtain an expansion vs. temperature curve by the absolute measurement method. Annealed samples were cut to dimensions of 5 x 5 x 50 mm approximately; the exact lengths were measured after cutting. The specimens were mounted in the dilatometer to obtain an expansion vs. temperature curve up to the dilatometric softening point. The rate of temperature increase was 4 ^{o}C/minute.

CHAPTER 4: RESULTS AND DISCUSSION

Series 1 Samples are subdivided into Series 1(A), 1(B) and 1(C) while Series 2 samples are subdivided into Series 2(A) and 2(B).

4.1 SAMPLES CONTAINING TWO OF THE FIVE OXIDES CeO_2, HfO_2, ThO_2, Y_2O_3 OR ZrO_2 (SERIES 1 SAMPLES)

4.1.1 Series 1(A) samples

Table 1 lists the compositions of Series 1(A) melts which contain Na_2O, B_2O_3 and two other oxides. These "silica replacing" oxides are CeO_2, HfO_2, ThO_2, Y_2O_3 and ZrO_2 and they were selected because they each have a good alkali resistance and a melting point of at least 2 400 °C . Part of each melt was quenched while the remaining portion was furnace annealed from 600 °C to room temperature and then heat treated to induce or enhance phase separation.

Heat-treated samples were then tested to determine whether they could be successfully leached in water. The surface areas of porous samples were measured. The void volume was determined for porous samples which did not disintegrate.

TABLE I: Compositions and pore characteristics of Series 1(A) samples

Sample Number		1	2	3	4	5	6	7	8	9	10
Composition calculated from the batch formula (weight per cent)	CeO_2	30	30	25	25	25	25	25	-	-	-
	ThO_2	-	-	-	-	-	10	10	-	-	-
	Y_2O_3	5	5	-	-	-	-	-	15	20	20
	ZrO_2	-	-	10	10	15	-	-	13	-	-
	HfO_2	-	-	-	-	-	-	-	-	10	10
	B_2O_3	56	56	56	56	52	56	56	61	60	60
	Na_2O	9	9	9	9	8	9	9	11	10	10
Crucible*		A	P	A	P	P	A	P	A	A	P
Appearance of quenched sample+		t	t	t	t	t	t	t	t	t	t
Heat treatment conditions (^0C/hrs)		700/2 +750/2 +790/2	600/2	650/3 +700/3	600/2 +650/2 +700/2	600/2 +650/2 +700/20	600/2 +650/4	600/2	650/3 +700/3	600/2 +650/4 +700/2 +650/4	600/2 +650/2 +700/2
Appearance after heat treatment		o	o	o	o	o	o	o	o	o	t
Leaching time (hrs)		72	72	72	72	72	72	24	72	72	72
Surface area (m^2/g)		55	157	±105	87	101	-	112	97	-	230
Void volume (ml/g)		0,10	0,28	-	Crumbles	0,18	-	0,19	0,18	-	0,41

Crucible* - A = Al_2O_3
P = Pt/Rh

Appearance+ - t = transparent
tr = translucent
o = opaque

TABLE I: Compositions and pore characteristics of Series 1(A) samples (cont.)

Sample Number		11	12	13	14	15	16	17	18	19	20
Composition calculated from the batch (weight per cent)	CeO_2	-	-	27	27	-	-	-	-	-	-
	ThO_2	-	-	-	-	13	13	13	13	15	15
	Y_2O_3	-	-	-	-	15	15	-	-	-	-
	ZrO_2	15	15	-	-	-	-	12	12	-	-
	HfO_2	15	15	8	8	-	-	-	-	15	15
	B_2O_3	60	60	56	56	61	61	64	64	60	60
	Na_2O	10	10	9	9	11	11	11	11	10	10
Crucible*		A	P	A	P	A	P	A	P	A	P
Appearance of quenched sample+		o	o	t	t	t	t	tr	o	o	o
Heat treatment conditions (^{0}C/hrs)		500/3 +550/3	600/2	600/2 +650/4	500/24 +550/24 +600/2	650/2 +700/2 +750/2	600/2 +650/2 +700/2	600/2 +650/2 +700/2	500/3	600/2 +650/2	600/2
Appearance after heat treatment		o	o	o	o	tr	o	o	o	o	o
Leaching time (hrs)		24	24	72	24	72	24	72	1	72	1
Surface area (m^2/g)		193	28	-	171	76	0,4	173	12	180	11
Void volume (ml/g)		0,87	1,08	-	0,21	0,13	0,06	0,29	0,17	0,4	0,32

Crucible* - A = Al_2O_3
P = Pt/Rh

Appearance+ - t = transparent
tr = translucent
o = opaque

Notes Concerning Samples in Table I

No. 1 Leached right through, maintained structure but mechanically weak and brittle.

No. 2 Leached right through.

No. 3 Only about 20 per cent leached and the leaching depth was about 0,3 mm. The heat treatment was changed to 650/3 + 700/6 + 750/3 and leaching was done for 96 hours but the sample was still only about 20 per cent leached. The surface area was measured as 21 m^2/g therefore the surface area of the leached portion was estimated as 21 x 5 = 105 m^2/g .

No. 4 Broke into small particles during leaching so an accurate void volume could not be obtained. About 80 per cent leached (leaching depth was about 0,8 mm) but the surface area was measured on a completely leached portion.

No. 5 After leaching was chalk-like and totally porous.

No. 6 The sample did not leach.

Nos 7 and 8 Leached right through, maintained structure but mechanically weak and brittle.

No. 9 The sample did not leach.

No. 10 Leached right through.

No. 11 Very soft after leaching and crumbled into small pieces.

No. 12 The leached product did not crumble but was brittle. A heat treatment of 600/2 + 650/1 followed by leaching for 24 hours was tried but the leached product was powdery and had a surface area of only 17 m^2/g .

No. 13 A thin outside layer was porous after leaching. The heat treatment was changed to 600/1 + 650/2 + 700/2 and leaching was done for 72 hours but the sample was still largely nonporous.

No. 14 Outer leached (porous) layer broke off and was measured for surface area.

Nos 15 16 and 17 Leached right through, maintained structure but mechanically weak and brittle.

Nos 18 19 and 20 Crumbled during leaching.

Successful leaching in water depended on the starting composition, heat treatment, physical thickness of the sample being leached and sufficient leaching time. All melts of Table I done in Pt/Rh crucibles could be totally leached within 72 hours if the slices of samples were not cut too thick. The same melts in Al_2O_3 crucibles generally had a slower leaching rate or resulted in a non-leachable material. This may be partly explained by the fact that these materials had a lower B_2O_3 and Na_2O content due to the Al_2O_3 which entered the melt. All alumina crucibles showed significant corrosion after melting. The melt may contain thirty per cent Al_2O_3 due to crucible

corrosion according to a chemical analysis of a melt reported by Hart et al. (1984). Another reason could be that the Al_2O_3 has a suppressing effect on phase separation for many of the compositions. The observation that Al_2O_3 has a suppressing effect on demixing in a number of glass systems, including the Na_2O-B_2O_3-SiO_2 system, is mentioned by authors such as Tomozawa. For leached products which had the same initial batch compositions, those melted in Al_2O_3 crucibles usually had larger BET surface areas than those melted in Pt/Rh curcibles (for example sample numbers 11 and 12). An exception is sample numbers 1 and 2 where the material melted in the Pt/Rh crucible had the larger surface area.

The samples which could not be leached (6, 9 and 13) had between 30 and 35 per cent of "silica replacing" oxides according to the batch formula plus a substantial amount of Al_2O_3 from crucible contamination. It appears that the lower the B_2O_3/Na_2O content the slower the leaching rate and for any particular sample the Na_2O plus B_2O_3 content must be above a certain level for leaching to occur. The B_2O_3 : Na_2O ratios of samples in Table I were all within the narrow range of 5,5 : 1 to 6,5 : 1. This range lies within the range of B_2O_3 : Na_2O ratios for Vycor glasses.

The samples which were leached were either opaque, translucent or transparent after heat treatment. The appearance of the sample could not be used to determine whether the sample could be leached or not.

A wide variety of compositions, whether melted in Al_2O_3 or Pt/Rh crucibles, had high surface areas. It is therefore clear that no one particular "silica replacing" oxide is responsible for the leached product having a high surface area. Only three leachable samples had surface areas of less than 20 m^2/gram. The only common factors of these three samples was that they were all melted in Pt/Rh crucibles and each contained 13 to 15 per cent ThO_2 according to the batch formulae.

4.1.2 Series 1(B) samples

Results from Series 1(A) glasses were used to prepare a few glasses (Series 1(B) glasses) to be investigated in more detail. Compositions of Series 1(B) samples were based on Series 1(A) samples which were melted in Pt/Rh crucibles and which had the highest surface areas. The amount of "silica replacing" oxides was increased in the corresponding Series 1(B) samples to help prevent excessive crumbling of the leached product. Also a composition containing Y_2O_3 and ZrO_2 was melted. Melts of these new compositions were furnace annealed from 600 °C and then heat treated and leached in distilled water.

The results are stated in Table II (samples 21 to 26). Five of the six materials were either partially or totally opaque after annealing or after the heat treatment step. Samples 21, 22 and 23 (Table II) had a crystalline appearance after the heat treatment. It therefore appeared that the amount of "silica replacing" oxides in these glasses had been increased to a level where a crystalline phase was readily formed in the glass during the heat treatment step. An X-ray diffraction pattern of sample 23 after heat treatment showed that the development of opacity was due to crystallization of CeO_2.

TABLE II: Compositions and pore characteristics of Series 1(B) samples

Sample Number		21	22	23	24	25	26
Composition calculated from the batch formula (weight per cent)	CeO_2	30	25	20	30	-	-
	Y_2O_3	-	-	-	10	15	15
	ZrO_2	-	-	-	-	-	13
	HfO_2	10	15	20	-	15	-
	B_2O_3	52	52	52	52	60	61
	Na_2O	8	8	8	8	10	11
Crucible		Pt/Rh	Pt/Rh	Pt/Rh	Pt/Rh	Pt/Rh	Pt/Rh
Appearance of annealed sample		brown glassy	brown glassy	brown glassy	brown glassy	glassy with opaque regions	glassy with opaque regions
Heat treatment conditions (^0C/hrs)		550/2 +600/2 +650/2	550/2 +600/2 +650/2	550/2 +600/2 +650/2	550/1 +600/2 +650/2	550/1 +600/2 +650/2 +700/1	600/2 +600/2
Appearance after heat treatment		opaque	opaque	opaque	brown glassy	glassy with opaque regions	glassy with opaque regions
Leaching time (hrs)		96	96	96	96	96	96
Surface area (m^2/g)		171	156	233	non-porous	248	384
Void volume (ml/g)		crum-bled	crum-bled	0,21	non-porous	0,21	crum-bled
Estimated leaching rate (mm/day)		0,3	0,3	0,6	very slow	0,6	0,6

All Series 1(B) samples could be leached except for number 24. Surface areas of the leached materials were higher than most of the samples from Table I. All samples leached slowly and if an unleached portion remained the outer leached layer crumbled off the unleached portion during drying. Series 1(B) samples which had the highest leaching rates also had the highest surface areas. This did not apply to Series 1(A) samples where the samples which required less time for leaching sometimes had relatively low surface areas.

4.1.3 Series 1(C) samples

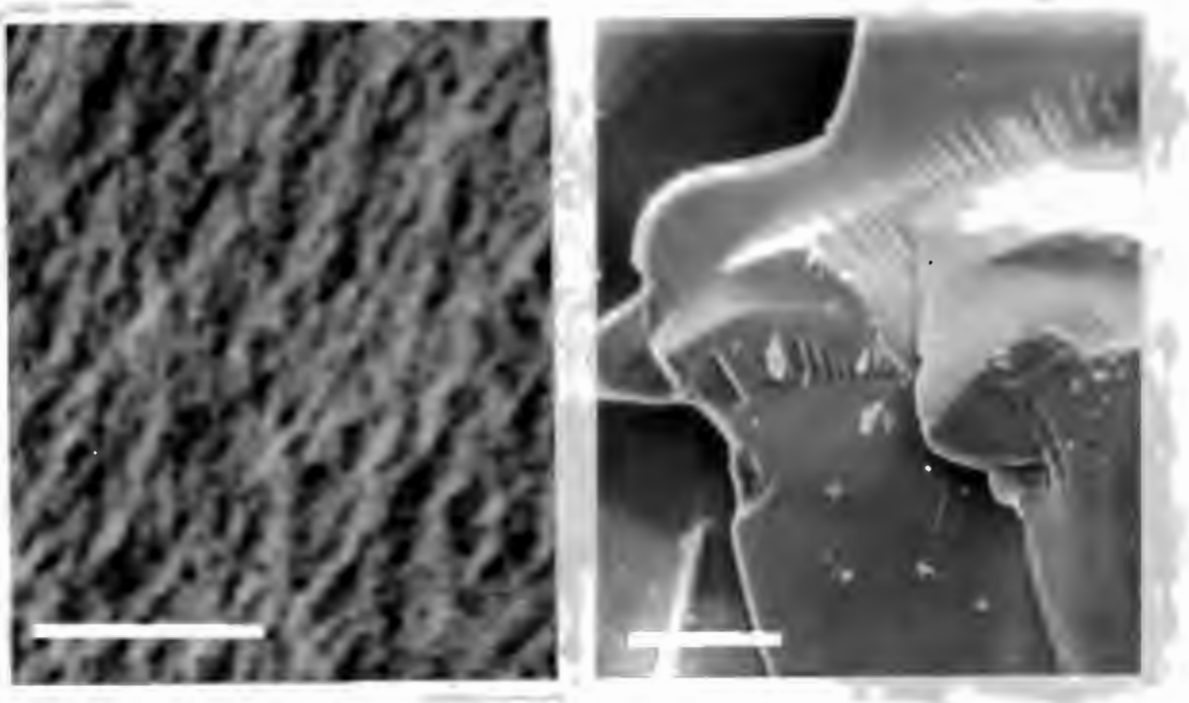
Samples 23 and 26 which both had high surface areas after heat treatment and leaching were chosen for further work. Annealed sample 26 contained small amounts of crystalline material which is likely to be either ZrO_2 or Y_2O_3 or both. It was therefore decided to decrease the ZrO_2 and Y_2O_3 content to 12 per cent each by weight and this composition was designated 27 and investigated instead of sample 26. Quenched glass of sample 27 was designated sample 27q. Other characteristics of these three glasses such as the alkali resistance and the chemical composition of leached samples were investigated. The starting compositions and results are shown in Table III. Dilatometric measurements showed that annealed sample 27 had a transformation temperature of 505 °C with a thermal expansion coefficient, $\alpha_{20-300} = 73{,}5 \times 10^{-7}\ °C^{-1}$. The same sample shows a slight rounding of its shape if heated to 600 °C for 24 hours and therefore 550 °C was chosen as the heat treatment temperature.

TABLE III: Compositions and properties of Series 1(C) samples

Sample number		27	27q	23
Composition calculated from the batch formula (weight per cent)	CeO_2	-	-	20
	HfO_2	-	-	20
	Y_2O_3	12	12	-
	ZrO_2	12	12	-
	B_2O_3	64	64	52
	Na_2O	12	12	8
Crucible		Pt/Rh	Pt/Rh	Pt/Rh
Heat treatment conditions (^0C/hrs)		550/3	quenched only	550/2 +600/2
Appearance after heat treatment		colourless, glassy	colourless, glassy	brown, glassy
Leaching time (hrs)		96	96	96
Weight loss due to leaching (per cent)		64	63	42
Mechanical state after leaching		brittle, crumbles	very brittle, crumbles	brittle, crumbles
Surface area (m^2/g)		381	413	243
Alkali resistance of leached sample (mg/dm^2)		$4,1 \times 10^{-3}$	$2,3 \times 10^{-3}$	$9,7 \times 10^{-3}$
Chemical analysis of leached material (weight per cent)	Y_2O_3	32,6	33,2	-
	ZrO_2	32,5	34,4	-
	B_2O_3	31,1	29,3	-
	Na_2O	0,5	0,5	-
X-ray diffraction result for leached material		non-crystalline	-	non-crystalline
Estimated leaching rate (mm/day)		0,6	0,6	0,6

Sample 23 had a surface area of 243 m^2/gram after a heat treatment of 550/2 + 600/2 and leaching (Table III). When the sample was given a further heat treatment step of 650/2 its appearance changed from glassy to opaque(Table II) due to the formation of crystalline CeO_2. When leached the opaque material gave a surface area of 233 m^2/gram. only slightly lower than the corresponding result for the glassy material.

It can be seen from Table III that the properties of samples 27 and 27q were similar. Figure 5(a) shows an electron micrograph of sample 27 after heat treatment and leaching. It is evident that the sample was phase separated, but due to the small size of the microstructure its morphology cannot be clearly seen.



(a) (b)

FIGURE 5: Scanning electron micrograph of a fractured surface of (a) sample 27 after a heat treatment at 550 °C for 3 hours and leaching (bar equals 1 μm); and (b) sample (a) after sintering at 800 °C for 5 minutes (bar equals 40 μm).

Sample 27 had a colourless transparent appearance, which showed no indication of phase separation. Doremus states that the amount of light scattering of a phase-separated glass depends on the size of the particles and the refractive index difference between the two phases. According to Fanderlik the refractive index of a glass increases as the molar refraction increases and as the molar volume decreases. The molar refraction is approximately the sum of the ionic refractions. B^{3+} is quoted as having a much lower ionic refraction than Y^{3+} or Zr^{4+}. In the case under consideration the ionic refractions of B^{3+}, Y^{3+} and Zr^{3+} play a major role in determining the differences in refractive indices. The borate-rich phase can therefore be expected to have a lower refractive index than the other phase or phases. Seeing that the phases have different refractive indices it therefore appears likely that sample 27 has a microstructural size that is too small to cause opalescence.

The surface area of 413 m^2/gram for quenched sample 27 was slightly higher than the corresponding value of 381 m^2/gram for the heat-treated sample 27. The lower surface area could be due to the growth of the microstructure by a coarsening process or to a change in composition of the soluble phase during the heat treatment. A change in the microstructure could not be confirmed by electron micrographs due to the small scale of the microstructure.

It is assumed that sample volume does not change significantly after leaching and a larger void volume is associated with a larger weight loss due to leaching. Most samples broke

down to small fragments during or after leaching and therefore void volume measurements could not be readily obtained.

The weight loss due to leaching can be used as an approximate check of the chemical analysis of the leached sample. In the case of samples 27 and 27q, having weight losses of 64 and 63 per cent respectively, the results are in general agreement with the compositions determined by ICP atomic emission spectroscopy and are listed in Table IV.

TABLE IV: Expected compositions of leached samples 27 and 27q calculated from weight losses due to leaching. It is assumed that 1 gram of starting glass is leached.

Oxide	Batch Composition (weight per cent)	27 leached		27q leached	
		(gram)	(weight per cent)	(gram)	(weight per cent)
Y_2O_3	12	0,12	33,3	0,12	32,5
ZrO_2	12	0,12	33,3	0,12	32,5
B_2O_3	64	0,12	33,4	0,13	35,0
Na_2O	12	0	0	0	0
	100	0,36	100	0,37	100

In Table IV the assumptions have been made that a negligible amount of yttrium and zirconium pass into the leaching solution and that all the sodium is leached out of the glass. One gram of the sample contains 0,12 gram of yttrium and zirconium according to the batch formula. Therefore a 64 per cent and 63 per cent weight loss means that the leached glasses 27 and 27q contain 0,12 and 0,13 grams of B_2O_3 respectively. These

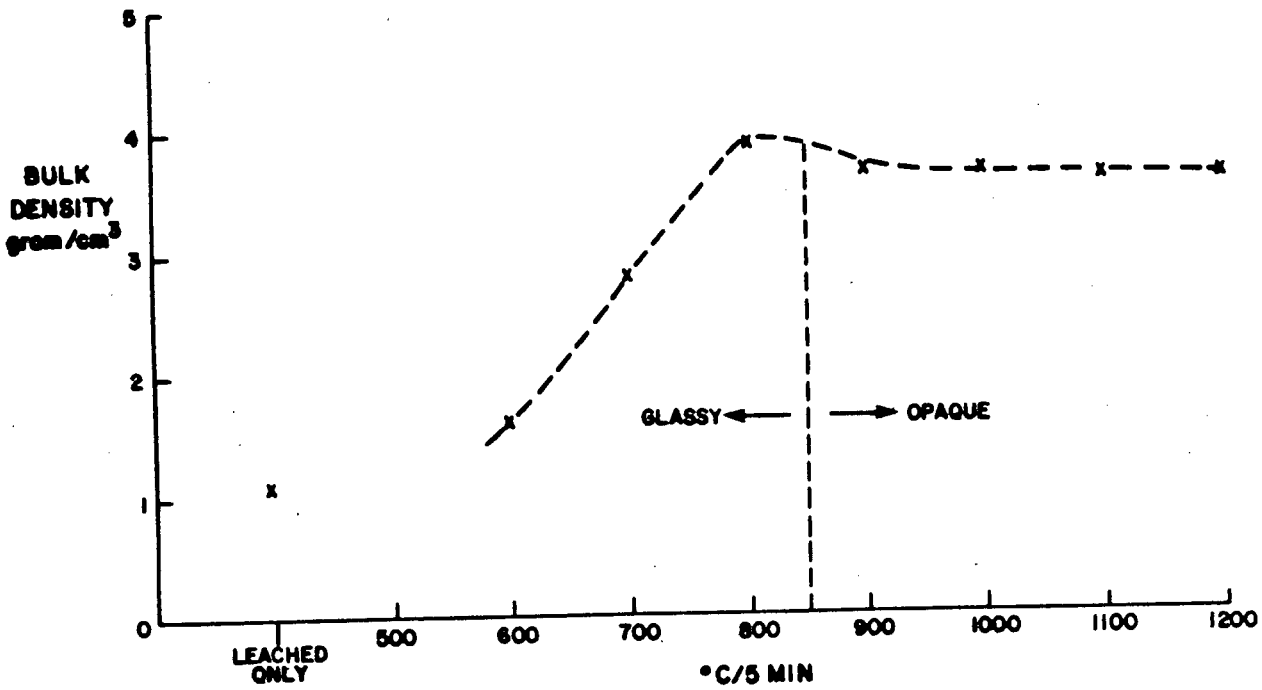


FIGURE 6: The estimated bulk densities after sintering of heat-treated and leached sample 27 (Table III).

B_2O_3 values are higher than those obtained from the chemical analyses. The difference may occur because the glass still contains a small amount of adsorbed water resulting in an over-estimation of the B_2O_3 content.

Sample 27 was sintered to determine the change in bulk density. Figure 6 shows the bulk densities of samples each sintered at different temperatures for 5 minutes. These measurements were carried out in accordance with methods detailed under sections 3.11 and 3.12.

The sample sintered at 800 °C had the highest density and for higher temperatures the densities were slightly lower. Samples sintered at 800 °C and below were transparent and glassy. Samples which were sintered at 900 °C and above had an opaque white appearance. An X-ray diffraction scan was done on a sample which had been sintered at 1 200 °C for five minutes. The diffraction peaks were due to ZrO_2 and YBO_3.

4.2 SAMPLES CONTAINING Ga_2O_3 AND Y_2O_3 (SERIES 2 SAMPLES)

4.2.1 Starting Compositions

Based on previous work by Res et al. (1984) the system Na_2O-B_2O_3 Ga_2O_3 showed quite an extensive glass forming region for the range of compositions studied. The batch (starting) compositions and appearance of quenched samples is shown in Figure 7.

In this study the work of Res et al. (1984) is extended by introducing Y_2O_3. Melts were made to establish the glass forming region for quenched samples covering a limited range of Na_2O-B_2O_3-Ga_2O_3-Y_2O_3 compositions. The starting compositions were calculated to contain between 5 and 20 per cent Na_2O by weight, with a total oxide content of 12,5 grams. Two groups of batches were prepared having Ga_2O_3:Y_2O_3 ratios of 3:1 by weight for one group and 3:2 for the other group. Figures 8 and 9 show the appearance of the quenched samples. Figure 8, with samples having Ga_2O_3:Y_2O_3 ratios of 3:1, showed a more extensive glass forming region and larger batches of some compositions were prepared for the evaluation of material characteristics. Figure 10 shows the batch compositions by weight

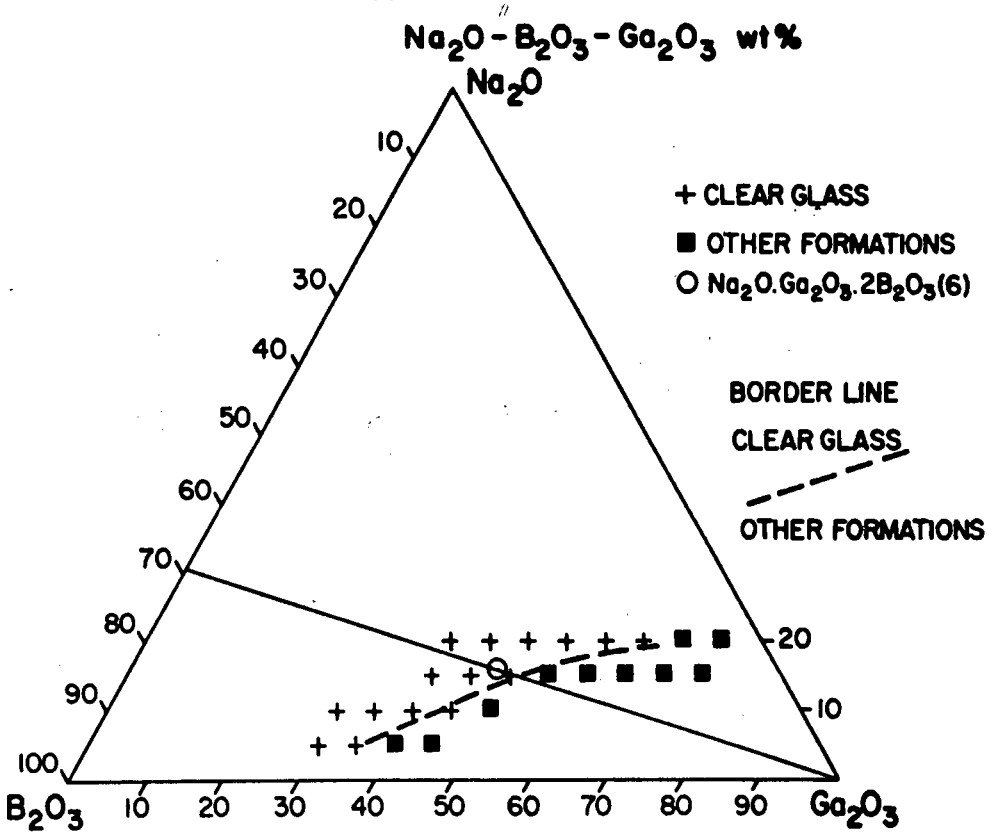


FIGURE 7: Starting compositions (by weight) and appearance of quenched melts of the Na_2O-B_2O_3-Ga_2O_3 system. The solid line represents Ga_2O_3-$Na_2B_4O_7$ phase compositions which were investigated by Rza Zade (reproduced from Res et al., 1984).

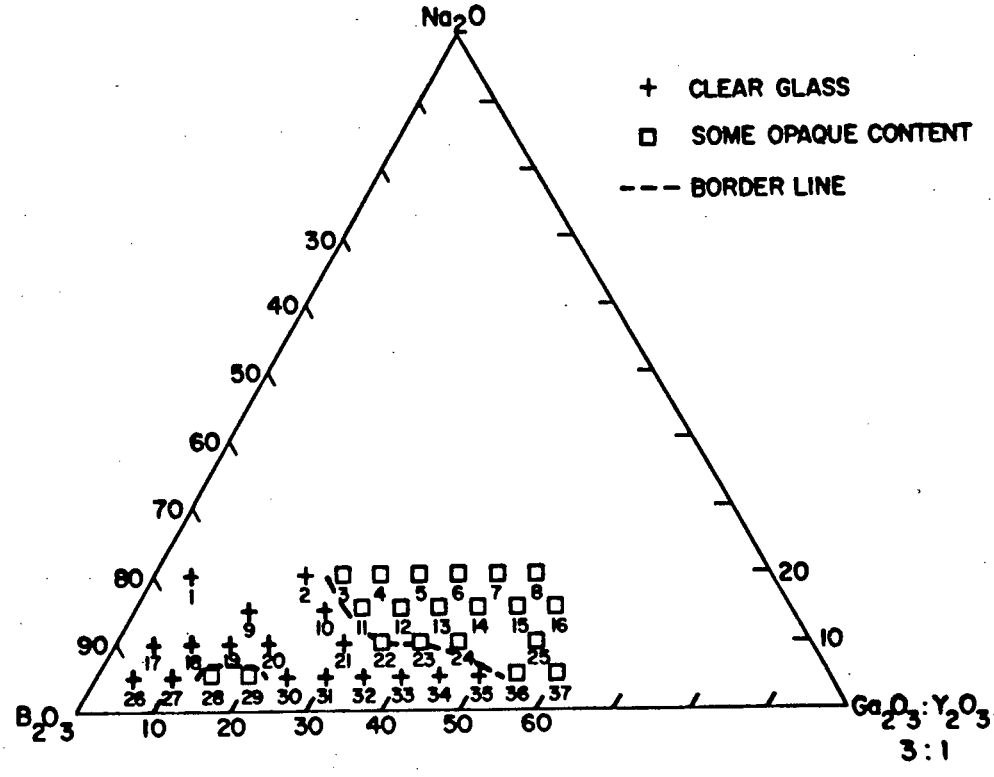


FIGURE 8: Starting compositions (by weight) and appearances of quenched melts of the Na_2O-B_2O_3-Ga_2O_3-Y_2O_3 system with a Ga_2O_3:Y_2O_3 ratio of 3:1.

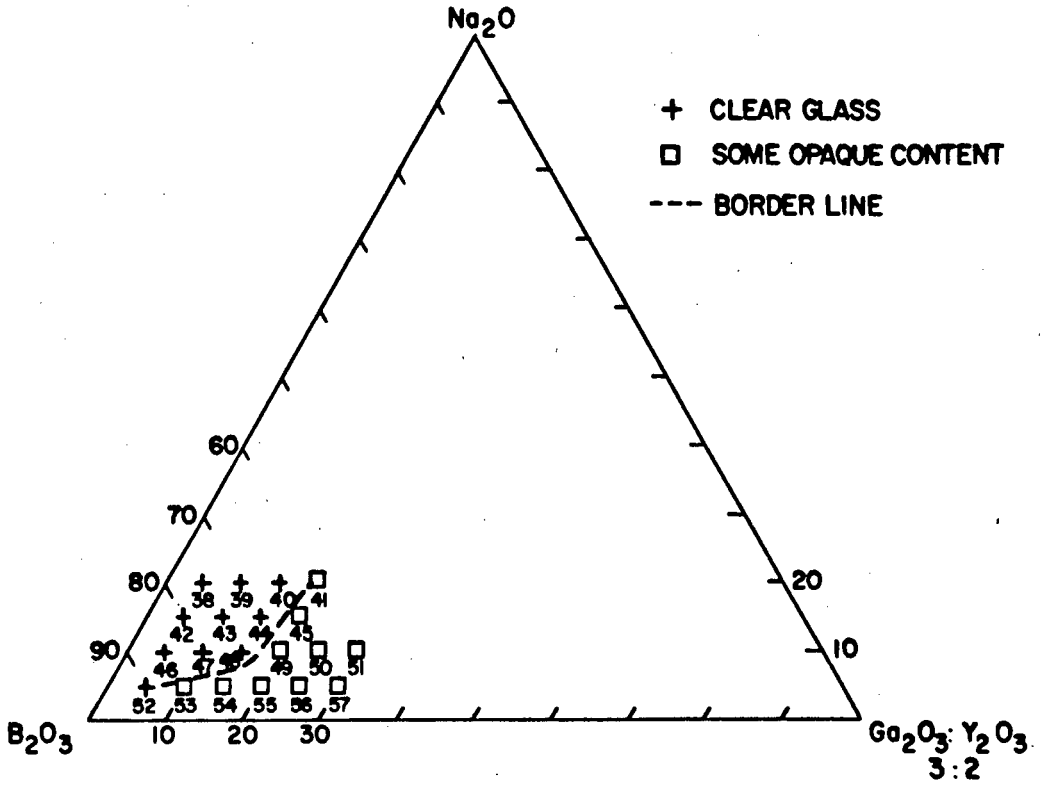


FIGURE 9: Starting compositions (by weight) and appearances of quenched melts of the Na_2O-B_2O_3-Ga_2O_3-Y_2O_3 system with a Ga_2O_3:Y_2O_3 ratio of 3:2.

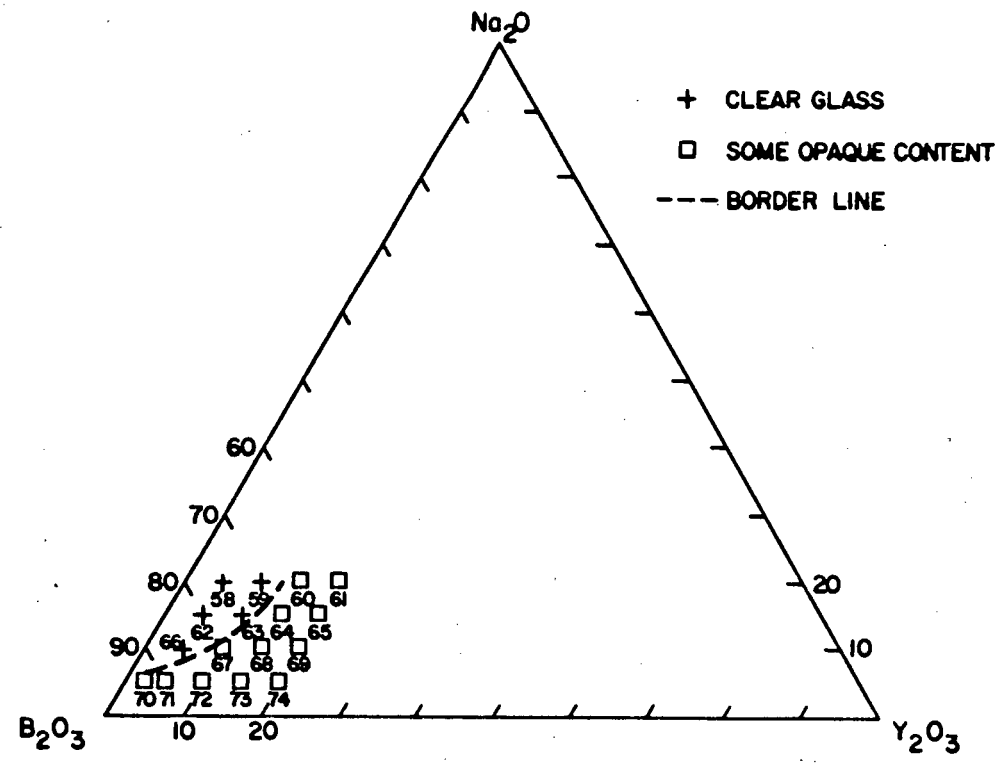


FIGURE 10: Starting compositions (by weight) and appearances of quenched melts of the Na_2O-B_2O_3-Y_2O_3 system.

and the appearance of quenched samples for a portion of the Na_2O-B_2O_3-Y_2O_3 system. For samples with a Na_2O content of between 5 and 20 per cent by weight only a small region gives glass of a transparent appearance.

During the compilation of Figures 8, 9 and 10 quenched samples which showed any traces of opacity or surface opacity were classified as having some opaque content.

4.2.2 Series 2(A) samples

Series 2(A) samples refer to glasses having a Ga_2O_3:Y_2O_3 ratio of 3 : 1. Figure 8 shows the starting compositions calculated from the batch formula. All quenched samples in Figure 8, whether classified as clear glass or material having some opaque content were mostly transparent glass. Nearly all materials classified as having some opaque content had surface opacity only, the bulk material being a transparent glass. The border line is thus debatable. However, samples 28 and 29 had some bulk opacity which was thought to be attributable to phase separation because X-ray studies of these samples gave no diffraction peaks. The development of the opaque appearance of these two samples occurred during cooling immediately after pouring the melts from the crucibles. Figure 11(d) shows phase separation in sample 29.

Sample numbers 33, 13, 21 and 35 of Figure 8 having Ga_2O_3 plus Y_2O_3 contents of 40, 40, 30 and 50 per cent respectively were chosen for the preparation of larger batches. These samples were selected because they had a relatively high content of "silica replacing" oxides and three of them were clear glasses.

Part of the melt was quenched and the rest furnace annealed from 550 °C to room temperature. The heat treatment temperatures (Table V) were about 20 to 80 °C above the glass transformation temperatures.

Table V shows some of the characteristics of samples of Series 2(A). Leaching times varied according to the physical thickness of the sample and its composition. A specimen of the quenched sample 37 was heat treated and tested for leachability, but remained non-porous after 72 hours in boiling water. For samples 33q, 33, 13q and 13 the expected weight loss due to leaching was calculated using the chemical analysis of the leached samples. For purposes of the calculation it is assumed that no yttrium is leached out, but that all the sodium is leached out.

Phase separation in transparent samples required a higher magnification for detection than for the opaque samples. Sample 33 showed a phase-separated microstructure under the electron microscope (Figure 11(a)) but the morphology is not clear due to the small microstructural size.

During the leaching of samples containing Ga_2O_3 and Y_2O_3 a white milky suspension formed in the leaching solution. This is particularly evident for samples 21q, 21, 13q and 13. For samples 33, 13q and 13 an amount of HCl was added to the leaching solution to form a 7 per cent HCl solution so that the suspension could be dissolved. Analyses of the resulting solutions showed gallium concentrations of well over 500 mg/ℓ and trace amounts of yttrium (see Table V). For sample 33 the suspension in the leaching solution was allowed to settle and

TABLE V: Compositions and properties of Series 2(A) glasses

Sample number		33q	33	13q	13
Composition calculated from the batch formula (weight per cent)	Ga_2O_3	30	30	30	30
	Y_2O_3	10	10	10	10
	B_2O_3	55	55	45	45
	Na_2O	5	5	15	15
Furnace annealing temperature (^0C)		quenched only	550	quenched only	550
Heat treatment conditions (^0C/hrs)		-	550/3	-	550/3
Appearance after heat treatment		-	transparent	-	transparent
Leaching time (hrs)		96	72	96	96
Weight loss due to leaching (per cent)		63	62	64	75
Alkali resistance of leached sample (mg/dm^2)		$2,9 \times 10^{-2}$	-	-	-
Surface area (m^2/g)		157	154	173	188
Chemical analysis of leached glass (weight per cent)	Ga_2O_3	54,9	54,4	38,9	31,9
	Y_2O_3	24,2	22,3	33,3	38,9
	B_2O_3	15,8	19,2	23,7	24,8
	Na_2O	0,1	0,5	0,8	0,4
Ga_2O_3:Y_2O_3 ratios of leached glass		2,27:1	2,44:1	1,17:1	0,82:1
Analysis of leaching solution (mg/litre)	Ga^{3+}	-	>500	>500	>500
	Y^{3+}	-	7	14	13
Weight loss due to leaching calculated from the leached glass composition (per cent)		61	57	71	75

TABLE V: Compositions and properties of series 2(A) glasses (Cont)

Sample number		21q	21	35	37q
Composition calculated from the batch formula (weight per cent)	Ga_2O_3	22,5	22,5	37,5	45,0
	Y_2O_3	7,5	7,5	12,5	15,0
	B_2O_3	60,0	60,0	45,0	35,0
	Na_2O	10,0	10,0	5,0	5,0
Furnace annealing temperature (^0C)		quenched only	550	550	quenched
Heat treatment conditions (^0C/hrs)		-	550/3	550/3	550/3
Appearance after heat treatment		-	transparent	transparent	opaque surface
Leaching time (hrs)		48	48	72	72
Weight loss due to leaching (per cent)		77	74	partly leached	not leached
Surface area (m^2/g)		143	168	110	non-porous
Chemical analysis of leached glass (weight per cent)	Ga_2O_3	-	-	51,8	-
	Y_2O_3	-	-	29,4	-
	B_2O_3	-	-	14,5	-
	Na_2O	-	-	0,1	-

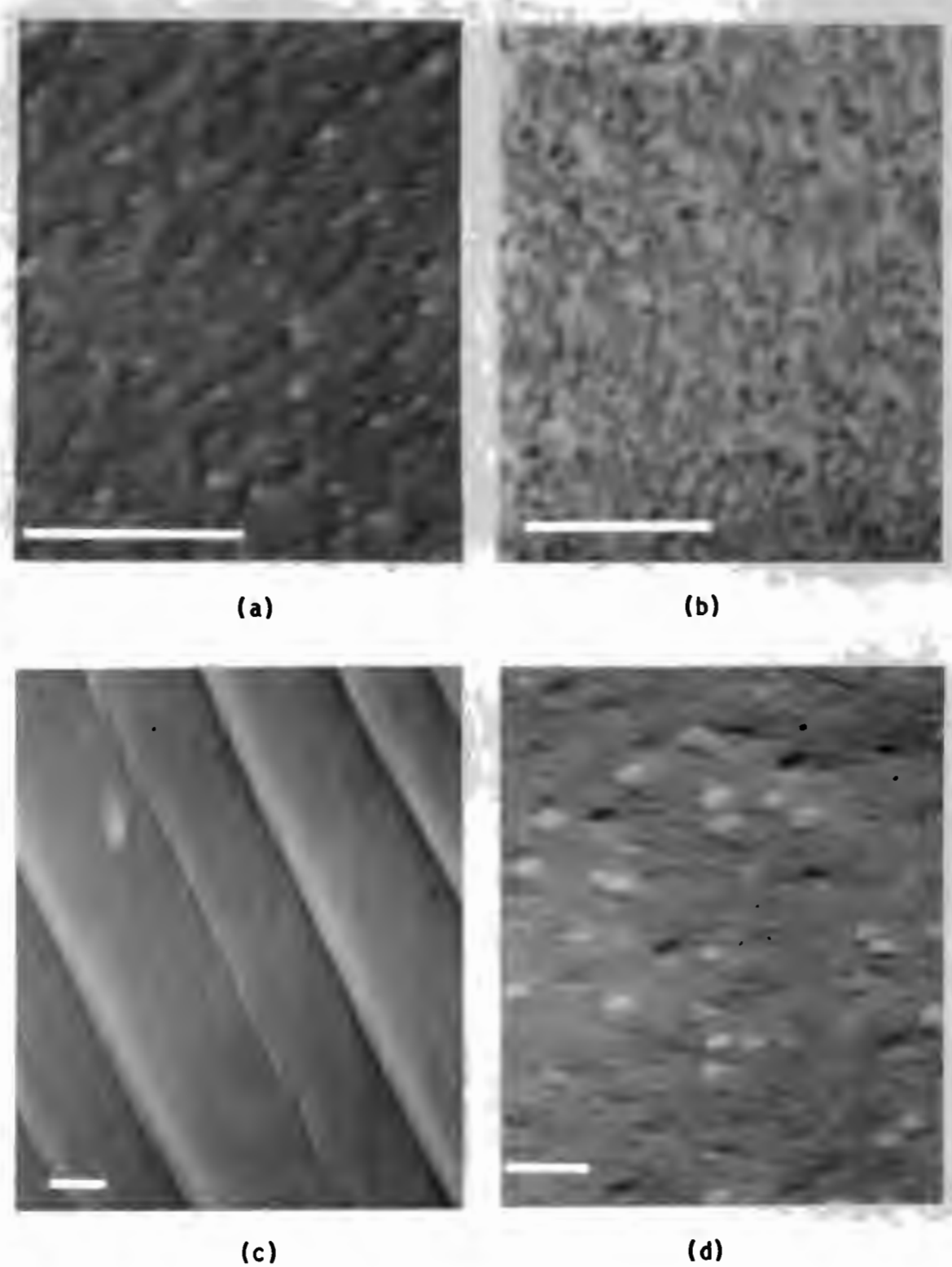


FIGURE 11: Scanning electron micrographs of fracture surfaces of (a) sample 33 after heat treatment at 550 °C for 3 hours; (b) sample (a) after leaching; (c) sample (b) after sintering at 800 °C for 5 minutes; and (d) quenched sample 29 (bars equal 1 μm).

an analysis of the resulting clear solution showed a gallium concentration of 272 mg/ℓ with the yttrium concentration being less than 1 mg/ℓ. This showed that during leaching a large amount of gallium was lost by dissolving into the leaching solution or by the formation of a suspension. The loss of yttrium during leaching was negligible.

The loss of gallium during leaching is confirmed by the chemical analyses of the leached glasses. For all analyses the Ga_2O_3:Y_2O_3 ratio is lower than the corresponding ratio for the starting composition of the batch. It is not certain whether the gallium lost during leaching originates from the boron-rich phase or another phase.

Samples 21q, 21, 13q and 13 (Table V) were noticeably heterogeneous after leaching. Some leached particles had a translucent appearance typical of porous glass while other pieces were opaque and powdery. The absence of peaks in an X-ray diffraction pattern of sample 21 after leaching showed that it was still glassy. This ruled out the possibility that the powdery portion could be due to the precipitation of a crystalline gallium compound.

The Ga_2O_2:Y_2O_3 ratio differs markedly for leached samples although the starting ratio is constant at 3 : 1. For samples 33q, 33, 13q and 13 lower ratios correspond to higher surface areas.

The results of the chemical analyses of leached glasses were similar for quenched and heat-treated glasses of the same

composition except 13. The different compositions of 13 and 13q may have resulted because 7,13 gram of sample 13q was leached in 200 mℓ of distilled water compared to only 3,89 gram of sample 13.

Sample 33 (Table IV) was sintered and the bulk density for different temperatures was determined. The methods used were the same as for sample 27 (Section 4.1.3). The results are shown in Fig. 12.

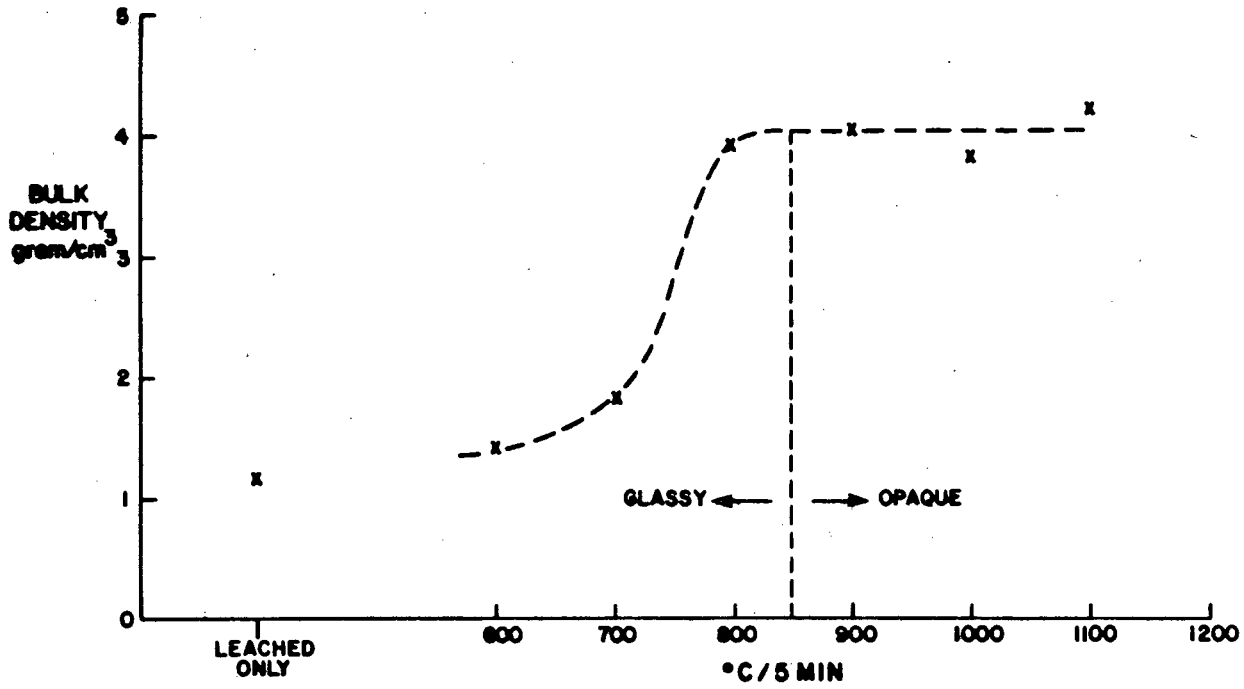


FIGURE 12: The estimated bulk densities after sintering of heat treated and leached sample 33 (Table V).

Samples sintered at 800 °C or less for 5 minutes were still glassy while those sintered at 900 °C or more were white and opaque. Figure 11(c) is for a sample sintered at 800 °C and

shows the "rib marks" typical of a glass fracture surface. An X-ray diffraction scan was done on a sample which had been sintered at 1 200 °C for 5 minutes. The diffraction peaks could be allocated to Ga_2O_3 and YBO_3.

The glass transformation temperatures were measured to help determine the heat treatment temperature for some of the Series 2(A) samples. The dilatometric results for Series 1(C) glass 27 and Series 2(B) glass 51 have been included in Table VI for comparison purposes.

TABLE VI: Dilatometric measurements

Annealed sample number	Amount of "silica replacing" oxides (weight per cent)	Transformation temperature (^0C)	Thermal expansion coefficient, α_{20-300} ($^0C^{-1}$)
27 (Y_2O_3, ZrO_2)	24	505	73×10^{-7}
21 (Y_2O_3, Ga_2O_3)	30	467	76×10^{-7}
33 (Y_2O_3, Ga_2O_3)	40	487	62×10^{-7}
35 (Y_2O_3, Ga_2O_3)	50	516	60×10^{-7}
51 (Y_2O_3, Ga_2O_3)	30	489	74×10^{-7}

4.2.3 Series 2(B) samples

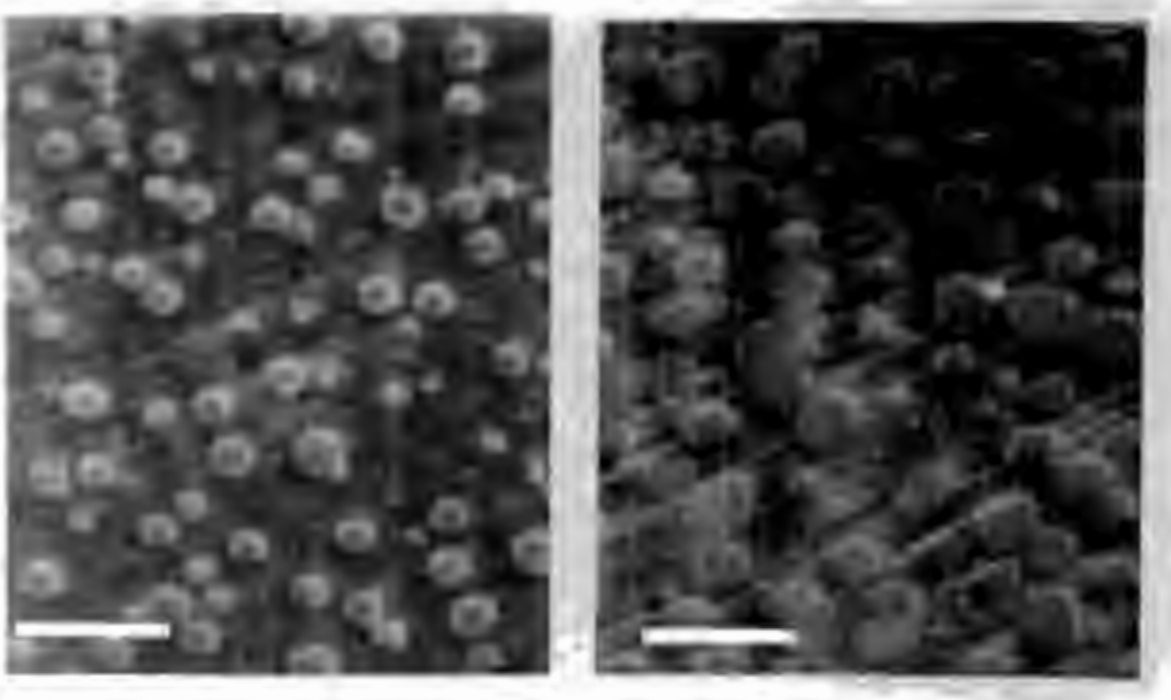
Series 2(B) samples refer to glasses having a Ga_2O_3:Y_2O_3 ratio of 3 : 2. Figure 9 shows the starting compositions calculated from the batch formula. Data on this series of glasses is given in Table VII.

Quenched samples 41, 45, 49 and 51 of Figure 9 had slight surface opacity. Quenched samples 54, 55, 56 and 57 were com-

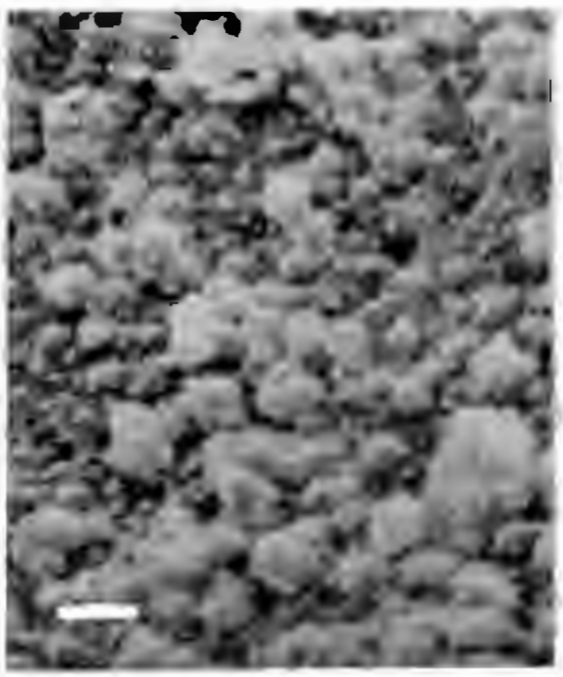
TABLE VII: Compositions and properties of Series 2(B) glasses

Sample number		51q	51
Composition calculated from the batch formula (weight per cent)	Ga_2O_3	18	18
	Y_2O_3	12	12
	B_2O_3	60	60
	Na_2O	10	10
Furnace annealing temperature (^0C)		quenched only	550
Heat treatment conditions (^0C/hrs)		-	520/3
Appearance after heat treatment		-	transparent
Leaching time (hrs)		48	48
Weight loss due to leaching (per cent)		69	67
Mechanical state after leaching		brittle, crumbles	brittle, crumbles
Surface area (m^2/g)		177	178
Chemical analysis of leached glass (weight per cent)	Ga_2O_3	31,3	30,5
	Y_2O_3	37,5	38,3
	B_2O_3	29,1	28,7
	Na_2O	0,3	0,5
Weight loss due to leaching calculated from the leached glass composition (per cent)		69	70
Analysis of leaching solution (mg/litre)	Ga^{3+}	>500	-
	Y^{3+}	1,5	-

pletely opaque. X-ray diffraction patterns of powdered samples 54 and 57 gave no diffraction peaks indicating that the opacity in these samples was due to phase separation. Figure 13(c) shows the porous structure which results after the leaching of quenched sample 57. A larger melt was made of sample 51 for evaluation of certain properties. Dilatometric measurements showed that annealed sample 51 had a transformation temperature of 489 °C with a thermal expansion coefficient, $\alpha_{20-300} = 74 \times 10^{-7}\ ^{\circ}C^{-1}$. Quenched sample 57 had an opaque, white appearance as a result of the phase separation which was predominantly of a discrete particle morphology (Figures 13(a) and 13(b)). The fact that these glasses are phase-separated in the quenched state suggests that these compositions phase separate while cooling. The portion of the sample in Fig. 13(a) is at an earlier stage of phase separation (due to a higher cooling rate) than the portion shown in Fig. 13(b). Lineal analyses were done on Figure 13(a) and 13 (b) (quenched sample 57) using equations given by Underwood. This revealed that the particles dispersed in the borate-rich matrix had volume fractions of 13 and 30 per cent and interfacial surface areas of 1,2 and 1,9 m^2/gram for Figs 13(a) and 13(b) respectively. These values are thought to be over-estimated due to the etching for specimen preparation. The BET surface area measurement for quenched sample 57 after leaching was 101 m^2/gram. This is a large increase over the interfacial surface area estimated from the electron micrograph. Two factors which could increase the surface area are: a) the gallium leached out of the sample which appeared to influence the surface areas of Series 2(A) glasses and, b) the possibility of colloidal particles from the borate phase which could vastly increase the surface area in a manner analogous to that for leached sodium borosilicate glasses.



(a) (b)



(c)

FIGURE 13: Scanning electron micrographs of quenched sample 57: (a) polished and etched surface taken near the outer edge of the sample; (b) polished and etched surface taken near the middle of the sample; and (c) fracture surface after leaching (bars equal 1 μm).

For sample 51 no microstructure could be detected under the scanning electron microscope for a fracture surface at a magnification of 50 000. The sample has a transparent appearance and the microstructure is probably too small to be resolved.

Solutions which were used to leach samples 51 and 51q were found to contain a white, powdery suspension. This had also been the case with Series 2(A) samples that had been leached.

An amount of HCl was added to some of the solution used to leach a quenched sample 51 to form a 7 per cent HCl solution so that the suspension could be dissolved for analysis. The result confirmed a large loss of gallium from the glass during leaching. For a quenched sample 57, the suspension in the leaching solution was allowed to settle, and an analysis of the resulting clear solution showed a gallium concentration of 53 mg/ℓ with a yttrium concentration of less than 1 mg/ℓ. Quenched samples 51 and 57 therefore behaved in a similar manner to the series 2(A) glasses during leaching in that a considerable amount of gallium but a negligible amount of yttrium was leached out.

CHAPTER 5: CONCLUSIONS

5.1 SAMPLES CONTAINING TWO OF THE FIVE OXIDES CeO_2, HfO_2, ThO_2, Y_2O_3 or ZrO_2

One of the main objects of this work was to produce leached materials having high surface areas. This was achieved for some of these materials.

For Series 1(A) materials (Table I) high surface areas were obtained for samples melted in both Pt/Rh and Al_2O_3 crucibles. Usually, but not always melts in Al_2O_3 crucibles resulted in higher surface areas than the same batch compositions melted in Pt/Rh crucibles. The wide range of surface areas in Table I show that surface areas are greatly influenced by glass composition. Therefore to obtain leached glasses of high surface areas certain experimentally determined compositions could be used. The influence of individual oxides upon surface area is not clear.

The more refined procedure of optimizing the heat treatment may be resorted to after a composition has been decided upon. Tables II and III (Series 1(B) and 1(C) materials) show the highest surface areas and they resulted from samples having a transparent, glassy appearance. This seems to correspond to the phase-separated glass having a small microstructure size. It was found that samples such as 23 and 27 had very high surface areas and good alkali resistance.

By altering the heat treatment of certain samples a crystalline phase was produced in the glass. For example, a CeO_2 phase was produced in sample 23 after a heat treatment at 550 °C, 600 °C and then 650 °C for 2 hours each. After leaching these partially crystalline materials a porous partially crystalline material having a high surface area was obtained.

The minimum leaching rates for glasses which had relatively high surface areas ranged from about 0,3 to 0,6 mm per day depending upon the composition, especially the B_2O_3 content. This compares with a leaching rate of about 1 mm per day which, according to Hood and Nordberg (1938) was required for a Vycor glass having a starting composition of 75 per cent SiO_2 and leached in three normal hydrochloric acid.

5.2 SAMPLES CONTAINING Ga_2O_3 AND Y_2O_3

Melts were made over limited ranges of the Na_2O-B_2O_3-Ga_2O_3-Y_2O_3 system having Ga_2O_3:Y_2O_3 ratios of 3:1 and 3:2. Melts with the higher Ga_2O_3 ratio of 3:1 resulted in clear glasses over a larger range of compositions than melts having the lower ratio. This was expected because Ga_2O_3 is a conditional glass former whereas Y_2O_3 has poor glass forming properties.

Leaching rates for Series 2 glasses (those containing Ga_2O_3 and Y_2O_3) varied greatly with the B_2O_3 content, being more rapid for samples having higher B_2O_3 contents. Series 2 glasses had a high surface area, but the alkali resistance of the sample which was measured was much lower than the values

obtained for Series 1 glasses. Quenched samples containing Ga_2O_3 and Y_2O_3 gave similar surface areas to the same samples which had been heat treated.

The gallium content of Series 2 glasses was partially leached out. Compared to Vycor glasses Ga_2O_3 may be considered to behave more like B_2O_3 than SiO_2 during leaching.

5.3 GENERAL CONSIDERATIONS

Although many of the properties of the glasses varied greatly with composition it was found that when samples having the same composition were compared their properties were similar whether they were quenched only or heat treated. This could be explained if phase separation occurred rapidly. In other words phase separation had already taken place to such an extent after quenching (by the method used in this work) that the heat treatment did not enhance it so significantly that the properties changed markedly.

The two leached glasses which were used for the sintering programmes displayed similar behaviour. There was a strong tendency towards devitrification due to the high proportion of non-glass forming oxides. Up to temperatures of about 800 °C for five minutes they remained glassy and above this temperature crystallization occurred.

The temperature of about 800 °C required to sinter the glass is lower than that of porous Vycor glass since the B_2O_3 content of both leached glasses 27 and 33 (analysed as 31,1 per cent and 19,2 per by weight respectively) was significantly higher than that of Vycor glasses.

In order to gain a greater understanding of the effect of composition and heat treatment on the microstructure of these materials it would be useful to study good electron micrographs. An attempt was made to obtain scanning electron micrographs for samples 27 (Series 1) and 33 (Series 2) but the resolution was poor due to the high magnifications required. It is suggested that a material with a coarser microstructure, but still having reasonably good properties could be studied with the aid of the electron microscope.

The mechanical strengths of the porous materials studied were low and all porous materials of Series 1(B), 1(C), 2(A) and 2(B) crumbled easily during or after leaching. This was partly due to crack formation during leaching. No attempts were made to improve the mechanical strengths of leached samples. To improve the mechanical strengths of leached samples and provide glass with better sintering properties it would be necessary to eliminate crack formation during leaching. Provided no cracks are present it might be possible to obtain an acceptable mechanical strength by preshrinking the porous sample at an elevated temperature.

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