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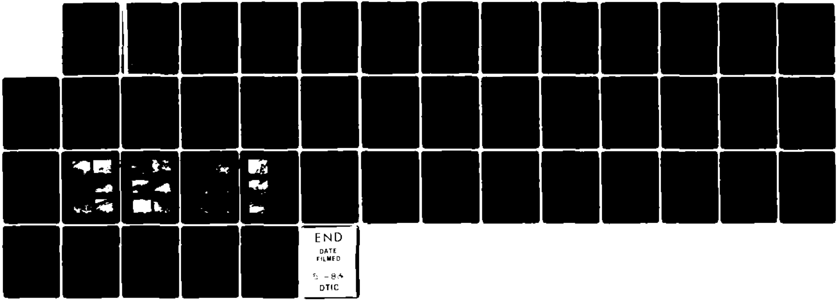

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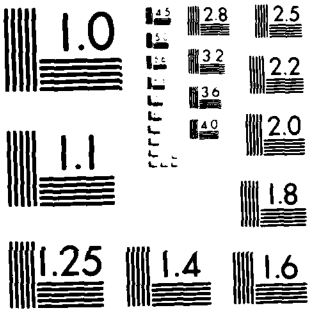

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SILICON OXYNITRIDE GLASSES AND GLASS-CERAMICS

PREPARATION AND PROPERTIES

Final Technical Report

by

R. ABRAMOVICI

JANUARY 1983

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United States Army
RESEARCH AND STANDARTISATION GROUP (EUROPE)
London - England

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The purpose of this work was to study the change of physical properties of certain glasses and the corresponding glass-ceramics as a consequence of incorporation of nitrogen.

Five series of glasses and their crystallized samples of Me-Si-Al-O-N (Me = Li, Ca, Mg, Ca+Mg, Mg+Li) system were prepared and studied. The criteria for selecting the composition within each system were: —(cont'd)

potential crystalline phases, castability of the melts below 1600°C, and in some cases, solubility of nitrogen in the melts.

Melting of the glasses was performed in alumina or slip cast silica crucibles, in air and also in nitrogen, with acceptable results as far as their corrosion resistance was concerned.

Nitrogen retention was of 61.7 - 74.2% for glasses melted in air (in covered crucibles) and 79.4 - 90.7% for those melted in nitrogen atmosphere.

Glass transition and dilatometric softening temperature, thermal expansion coefficient and microhardness were measured. The crystallized samples were examined also by XRD and SEM.

Qualitative observations and the quantitative results showed that the melt viscosity, glass transition and dilatometric softening temperatures as well as the microhardness increase, while the thermal expansion coefficient decreases with the incorporation of nitrogen.

Within the range of nitrogen concentration up to 5 at. % the effect of nitrogen content on phase composition manifested itself only in two cases, when it favoured eucryptite and crystobalite crystallization, respectively.

The nucleating action of nitrogen was noted only for glasses in the Mg-Li-Si-Al-O-N stem.

The property most strongly influenced by the incorporation of nitrogen was the microhardness. The highest microhardness values were found for glasses and crystallized samples in the Ca-Si-Al-O-N system.

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SILICON OXYNITRIDE GLASSES AND GLASS-CERAMICS
PREPARATION AND PROPERTIES

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The property most strongly influenced by the incorporation of nitrogen was the microhardness. The highest microhardness values were found for glasses and crystallized samples in the Ca-Si-Al-O-N system.

Key words

Glasses, - oxynitride, siliconoxynitride.
Glass-Ceramics, - oxynitride, Siliconoxynitride.
Sialons.

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1. Introduction.

The first papers concerning physical and chemical solubility of gaseous nitrogen in glass melts are due to Mulfinger et al./1-3/, who found that the highest incorporable amount of nitrogen is of about 1 wt.%.

Elmer and Nordberg achieved a higher nitrogen concentration (3%) by nitriding a porous high silica glass in a stream of ammonia at 500-1000^{0}C/4/.

Generally higher nitrogen concentrations (shown in parantheses together with the various systems) were obtained by Loehman (7 at % N, Y_2O_3 - AlN-SiO_2 and 3,62 wt % N, Mg - Si - Al - O - N)/5,6/, Shaw and Thomas (3,6 wt % N, MgO - SiO_2 - Si_3N_4) /7/, Jankowski and Risbud (2,13 wt % N, Si-Na-B-O-N)/8/, Leedecke (6,3 wt % N, Y-Si-Al-O-N) /9/ by using Si_3N_4 or AlN as the nitrogen source.

Glasses of the Mg-Si-Al-O-N and Y - Si - Al - O - N. systems, containing up to 10 wt % nitrogen, were obtained by Jack /10,11/.

Larger amounts of nitrogen can be incorporated by increasing the nitrogen overpressure.

By performing the melting in a nitrogen overpressure of 80 atm, Makashima et al. obtained a glass of the La - Si - O - N system, containing 18 at % N /12/.

Wusirika and Chyung report obtaining some glasses of the Si-Al-O-N system, with various oxides and fluorides added, the ratio of Si_3N_4 introduced into the batch varying between 10 and 46% (3,99 - 18.37 wt%N) /13,14/.Considering the about 90% retention of nitrogen in the glasses indicated by the authors, the nitrogen concentration obtained is high, especially if the fact,that melting of glasses was performed without nitrogen overpressure,is also taken into account.

Nitrogen solubility depends on nitrogen overpressure during melting and also on chemical composition of the melts. Thus, according to Loehman, it is maximum 10 wt% N in the Mg - Si - Al- O - N and Ca - Si - Al- O - N.systems (without high nitrogen overpressure), compared to maximum of 4 wt% N. in the Y - Si - Al - O - N system /15/.

The interest for oxynitride glasses was motivated by the notable change in their physical properties caused by introduction of nitrogen.

Loehman reports a systematic correlation between the amount of nitrogen incorporated into oxynitride glasses and the changes in their physical properties /5,15/. Thus, viscosity, glass transition temperature and refractive index increase, while the thermal expansion coefficient decreases with increasing nitrogen content.

A similar increase in microhardness was found by Shillito et al./16/.

This change in properties is attributed to the fact that substitution of oxygen by nitrogen

$$\equiv Si - O - Si \equiv \quad \cdot \quad \equiv Si - N \begin{matrix} Si \equiv \\ Si \equiv \end{matrix}$$

must lead to a higher average coordination number of the non-metal atoms and the increased crosslinking should produce a more rigid glass network /3/.

Replacement of oxygen by nitrogen in the Si-Al-O-N systems leads (up to a given nitrogen content) to an inlargement of the glass forming region and also to a lowering of the liquidus temperature /17-20/.

The effect is similar to that occuring when an equivalent amount of SiO_2 is added. Thus, in the $MgO-Al_2O_3 - SiO_2$ system, adding 10 wt% Si_3N_4 induces the same decrease of liquidus temperature (200^oC) as adding 10% SiO_2.

As a consequence of the interest in oxynitride glasses of various systems, work was also started on the corresponding glass-ceramics, although the number of papers published so far in this direction, is still small.

Jack shows that obtaining glass-ceramics in which the crystalline phases are refractory nitrides and oxynitrides is interesting from the scientific as well as from the technologic point of view /18/.

The early work performed on this subject focused on the crystallisation of glasses from systems which are important for the syntering of silicon nitride and, in the first place, of those from the Y-Si-Al-O-N system.

Leedecke and Loehman noted that in a series of glasses from this system. $Y_2 SiO_7$ crystallizes as the predominant phase /6,9/.

In addition, other crystalline phases like Y_2SiO_5, $Y_3Al_5O_{12}$, $Al_6Si_2O_{13}$ and Si_2N_2O also appear depending on the heat treatment regime and the nitrogen content. Preferential crystallization of $Y_2 Si_2O_7$ implies the enrichment in nitrogen of the residual glass phase. Only electric measurements were performed on the obtained glass ceramics.

Schaw and Thomas studied the crystallization behaviour of some glasses from the Mg-Si-O-N system and also found that most of the nitrogen was in the matrix phase /7/. The glasses of this system are candidates for obtaining "useful glass ceramics".

Wusirika and Chyung investigated a wide range of oxynitride glasses in order to obtain glass-ceramics /13,14/. A large number of modifiers M_xO_y was added to compositions of the Si-Al-O-N system in order to broaden the glass forming regions and to make glass processing easier.

In the glasses obtained, up to one of seven oxygen atoms could be replaced by nitrogen.

The oxynitride glasses were self nucleating and formed after heat treatment fine-grained glass-ceramics. Consequently, the addition of conventional nucleating agents such as TiO_2. ZrO_2 or SuO_2 was not required to cause crystallization in situ.

At low levels of nitrogen, X-phase crystals were observed, whereas at high levels of nitrogen, Beta-silicon nitride was found to crystallize from these glasses.

It must be noted that amoung the 46 glasses obtained in the framework of the patent of Chyung et al/14/, 39 were melted in air in silica crucibles under nitrogen atmosphere.

2. Objectives of the Work

The aim of the present work was to study the change in physical properties of some glasses and their corresponding glass-ceramics as a result of incorporation of nitrogen.

The prepared parent glasses (without nitrogen) are of the Me-Si-Al-O system, where Me is Li, Ca, Mg, Li+Mg and Ca+Mg.

In order to examine the effect of nitrogen, glass samples were prepared with and without nitrogen additions to the batch.

The following subsidiary points were also studied :

- the possibility of obtaining glass-ceramics from oxynitride glasses without adding nucleating agent;
- melting some of the oxynitride glasses in air, giving up the nitrogen atmosphere;
- melting the oxynitride glasses in alumina or silica crucibles instead of very expensive boron nitride or molybdenum ones.

3. Materials used.

- Belgian sand "SIBELCO" (99.82% SiO_2).
- Calcined aluminum oxide, analytical reagent, BDH Chemicals Ltd Pools, England.
- Lithium hydroxide-1- hydrate, Riedel-De Haen A.G. West-Germany (99.85% $LiOH.H_2O$).
- Magnesium oxide p.a. min. 97% MgO, Merck, West-Germany.
- Calcium carbonate precip., extra pure. Merck, West-Germany.
- Silicon nitride H. Stark, Berlin (silicon nitride - 97%; nitrogen - 38.4%).
- Lithium fluoride, analytical reagent, E. Greiner et Co. New-York.

4. Experimental Procedures.

Dry mixing of batch ingredients was performed during four hours in a polyethilene lined ball mill. The weight of the batches was of 160-180g.

Before melting, the $CaCO_3$ containing batches were decarbonated at 1100^{0}C.

The Si_3N_4 containing batches were melted in a vertical tubular furnace with Superkanthal heating elements.

The melting temperatures and times were 1550-1600^{0}C and 15-16 hours, respectively. The soaking time was one hour.

The parent glasses (without nitrogen) were melted in a box type furnace with Superkanthal heating elements at 1540-1570^{0}C, during 14-15 hours.

The soaking time was one hour in all cases.

Several researchers observed a high corrosion of conventional oxide-based crucibles by oxynitride melts. They reported the use of BN, BN coated graphite or graphite crucibles /6,10,11,17/. Silica crucibles were used by Chyung et al for melting of many oxynitride glasses in air.

The melting of our glasses was performed, depending on the furnace atmosphere and the batch composition, in alumina and silica crucibles. The crucibles used and the melting atmosphere will be indicated bellow for each group of glasses separately.

Nitrogen was introduced through an opening in the top of a sintered alumina bell and a slightly positive nitrogen pressure was maintained in the system.

The melts were poured into steel molds to yield slabs (67x6x5mm) which were immediately transferred into a furnace for annealing at 500-700^{0}C, according to the glass composition.

The heat treatment for nucleation was performed at temperatures 50^{0}C above the glass transition temperature /21/, which were determined from the DTA curves (first endothermic peak) and the dilatograms, respectively.

For crystallization,the nucleated samples were heated at 1-5 temperatures.

The nitrogen content was determined in the glass richest in nitrogen of each group. The nitrogen determinations were performed by the Metallurgical and Process Research and Development Laboratory of the Oregon Metallurgical Corporation. A model TC-30 Leco Oxygen-Nitrogen Analyzer was employed. The samples were wrapped in platinum foil which act as a catalyst in evolving the gases. They fused in a graphite crucible in a impulse furnace. The evolved gases, carried in a helium stream, were separated and passed over a thermal conductivity cell which with the associated electronic circuits give the nitrogen content with a digital readout.

The glasses were subjected to DTA and dilatometric and microhardness determinations.

The microhardness tests were performed by means of a "L L" Tukon Microhardness Tester with 136^0 Diamond Pyramid Identer (Vickers) under 100 gr load with contact time of 18 sec.

On crystallized samples, XRD, SEM, dilatometric and microhardness determinations were performed.

5. Compositions in the SiO_2 - Al_2O_3 - Li_2O Basic System.

The selection of the glass composition of this system was affected by the relatively low melting temperatures, on one hand, and by the capability to crystallize characteristic to glasses with high lithium content, on the other hand.

It was started with a glass composition corresponding to the low temperature entectic (975^{0}C). The compositions of the batches are shown in Table 1,I.

Taking into account the above mentioned high crystallization capability of these glasses and also the hints from the literature concerning the self-nucleating capability of oxynitride glasses /13/, no nucleating agent was used.

Glasses 1, 1.1 and 1.2 were melted in alumina crucibles. Melting of Glasses 1.1 and 1.2, containing Si_3N_4, was performed in nitrogen atmosphere.

The melting temperature was of 1500^{0}C (Glass 1) and 1600^{0}C (Glasses 1.1 and 1.2). During the melting, foam formation was observed. Foam formed at a higher rate for silicon nitride containing batches, preventing formation of compact glass samples.

In order to prevent the foaming and the resulting overflow of the melt from the crucibles, several heating schedules were experimented with. Finally, the problem was overcome by :

- slowly rising the temperature up to 1300^{0}C and maintaining it during 1 hour,
- replacing, initially used lithium carbonate by lithium hydroxide,
- pressing the batch into pellets,
- Glasses 2 and 2.1 with nucleating agent TiO_2 were also studied. Their batch composition is shown in Table 1,I.

Because the melt strongly corrodet the alumina crucibles, silica crucibles were used, and as a result, melting was performed in air. The melting temperature was of 1550^{0}C.

Pouring behaviour and visual description of the glasses thus obtained are given in Table 2.I.

Heat treatments for nucleation and crystallization were done at the temperatures shown in Table 3,I, in which the aspect of the samples after treatment is also given. The soaking time was 2 hours for all the temperatures.

The nitrogen content was determined in Glasses 1.2 and 2.1 (Table 4). Chemical analysis shows that nitrogen retention in Glass 2.1 (61,7%) is lower that in Glass 1.2 (85%), because the first one was melted in air /13,14/.

The determinations mentioned at Point 4 were performed on both glassy and crystallized samples.

XRD- analysis (Table 5,I) performed on all the 5 glasses before heat treatment showed them to be non crystalline except for some regions in Sample 1.2 which cooled more slowly during the pouring and in which the presence of eucryptite, silica O form,was detected.

The glasses treated for nucleation, were non crystalline.

Because of frequent overlaping of the characteristic XRD lines seen for the crystallized samples 1, 1.1, and 1.2, a clearcut distinction between crystalline phases was sometime difficult and has to be taken with some caution.

In the crystallized Glasses 1, 1.1, 1.2, the main phases are lithium metasilicate and spodumene. Along with them,and in smaller amounts,$Li_2O.Al_2O_3.6SiO_2$ and eucryptite also appear (the later, only in samples 1,1 and 1.2 containing nitrogen).In Samples 2 and 2.1, the only crystalline phases are Beta-eucryptite and rutile.

Crystallized phases with nitrogen such as nitrogen-mullite, silicon nitride or siliconoxynitride were not detected.

The microstructure of the crystallized glasses with TiO_2 addition differs markedly from that of crystallized glasses without it.

Compared to Sample 1 (without nitrogen), Sample 1.2 (with nitrogen) show a more advanced crystallization. The size of the crystals is similar to that found in Sample 2 and 2.1.

The data concerning glass transition temperature, dilatometric softening point, thermal expansion and microhardness, in the glassy, as well as in the crystalline state, are shown in Table 6,I.

From visual observations during pouring of the glasses and from the results of the property measurements, the findings were as followed.

The nitrogen containing melts are more viscous and more difficult to pour than the corresponding parent glasses.

Glass transition and dilatometric softening temperatures of Glasses 1, 1.1, 1.2, increase with nitrogen incorporation.

As expected, thermal expansion decreased as nitrogen was incorporated into Glasses 1, 1.1 and 1.2. The same regularity, but in a more distinct way is observed also for the corresponding crystallized samples. The stronger decrease of thermal expansion of the glass-ceramics suggests the influence of the nitrogen content on the enhancement of crystallization of phases which reduces the thermal expansion coefficient (eucryptite). Thus, according to the results of the XRD, in samples

1.1 and 1.2 (with nitrogen) eucryptite is present while it is absent in Sample 1 (without nitrogen).

Introduction of TiO_2 into Glasses 2 and 2.1 induces, after crystallization, a significant decrease in thermal expansion ($\alpha_{25-325} = 3.3\times10^{-7}$ for both samples), which is due to the formation of eucryptite as the main phase.

On the other hand, the determined thermal properties of these glasses, before, as well as after heat treatment, are only slightly affected by the introduction of nitrogen.

The presence of nitrogen results in increased microhardness for all the five studied glasses and for their crystallized products. After crystallization, the samples have a higher microhardness than in the corresponding glasses, except for the crystallized Sample 2, which had a lower microhardness than in the glassy state. This has to be related to the presence of cracks observed around the indentations.

Conclusions.

Incorporation of nitrogen resulted in an increased viscosity of the melts.

The presence of nitrogen influences, to a limited extent, the phase composition of crystallized glasses without nucleating agent , by favouring eucryptite crystallization. Possibly, this influence also exists in the case of glasses with TiO_2, where it is, however, masked by the stronger one of the nucleating agent.

The microstructure of nitrogen containing samples is roughly similar to that of samples without nitrogen. All the crystallized samples are finely grained (< 2 microns), but crystallization is more advanced in samples with TiO_2, those without nucleating agent being characterized by a higher content of residual glass.

Introduction of nitrogen influences to a different extent the thermal properties (thermal expansion, glass transition and dilatometric softening temperatures) of samples, with and without TiO_2. The change of these properties is stronger for the former and weaker for the latter,which has to be related also to the lower nitrogen content in samples with TiO_2, melted in air.

Microhardness increases with the introduction of nitrogen for both kinds of glasses and for the corresponding glass-ceramics.

Among the results, the following ones are emphasized :

- microhardness of 942 kg/mm^2 (Glass-ceramic 1.2),
- thermal expansion coefficient (25 600°C) of 8.7×10^{-7}(Glass-ceramics 2 and 2.1).

6. Compositions in the SiO_2 - Al_2O_3 - MgO Basic System.

The glass composition was chosen on the one hand to obtain, after heat treatment, cordierite as the principal crystalline phase, and on the other hand, to achieve melting below 1600°C.

A series of tests performed in a wide range of compositions of this system showed that the glasses melted at this temperature were too viscous and inhomogeneous even when only small amounts of Si_3N_4 were added.

In order to lower the melting temperatures of the glasses and also to improve their crystallizing capability, TiO_2 or LiF were introduced into their composition (see Table 1, II).

The first melting trials showed that alumina crucibles were strongly corroded, which caused leaking of most of the melt. Consequently, silica crucibles were used. To avoid their destruction as a result of reduction of SiO_2 to SiO, the melting of nitrogen containing batches was performed in air, the crucibles being covered/13,14/. Chemical analysis of Glass 3.2 obtained in this manner showed a nitrogen retention of 74.2 % (see Table 4).

Melting of Si_3N_4 and TiO_2 containing Glasses 4.1 and 4.2 was also tried in the same crucibles in nitrogen atmosphere. Although some corrosion of the crucibles was noted, their integrity was preserved.

The dissolved amount of SiO_2 was not considered to significantly modify the chemical composition of the melt.

Nitrogen retention was determined to be 87,7 % for glass 4.2 (see Table 4). Within each group of glasses a parent glass and two glasses with different nitrogen content were prepared.

The melting temperature was 1600°C in all cases. The melting atmosphere is shown in Table 1.II.

The glass samples were annealed at 700°C.

Pouring behaviour and a visual description of the glasses are given in Table 2,II.

Heat treatment for nucleation and crystallization were performed at the temperatures given in Table 3, along with the appearence of heat treated samples. As in the previous cases, soaking time at the various temperatures was of 2 hours.

XRD analysis (Table 5,II) showed that the non heat treated samples, including Glass 3, which had several very thin, opaque bands on the surface, did not show signs of crystallization. It seems that,in the case of Glass 3.1, crystallization occured to such a small extent, it could not be detected by XRD.

The glasses were X-Ray amorphous also after heat treatment for nucleation, even in those cases when a slight change in colour was observed (Glasses 3.1 and 3.2).

In all the crystallized glasses, cordierite was the main crystalline phase (see Table 5,II). Along with it, there was spodumene in samples with LiF addition (Samples 3, 3.1, 3.2) and rutile and crystobalite in those containing TiO_2 (Samples 4, 4.1, 4.2).

The microstructure of Samples 3, 3.1 and 3.2 was inhomogeneous, being characterized by two kinds of sectors with different aspect : some with advanced crystallization (Fig.5), the other with glassy character (Fig.6). Most of the crystals were over 2 microns in size.

The aspect of the microstructure as well as crystal size are not the typical ones for a glass ceramic. It appears that for the given compositions and nitrogen content, this did not exert the nucleating action suggested in /13/.

The electron micrograph (Fig.7) shows the fracture surface of the nucleated Glass 4. Its appearance is homogeneous, with barely visible roughness. After crystallization, crystalls smaller than 2 microns are seen as well as an approximately equal amount of residual glass (Fig.8). Crystallization of Samples 4.1 and 4.2 (with nitrogen) was more advanced and more fine. (Figs. 9 and 10).

Since all the three Glasses 4, 4.1 and 4.2 contain TiO_2, then the finer crystallization of Samples 4.1 and 4.2 must be attributed to the presence of nitrogen. Considering the comments about Glasses 3, 3.1 and 3.2, it seems that for the same nitrogen content, its influence on crystallization depends on the composition of the glasses. During pouring, Glasses 3, 3.1 and 3.2 were found to be more fluid than those with LiF (Glasses 4, 4.1, 4.2), but in both cases, it was noted that viscosity was higher (although to an unequal extent) when the nitrogen content was higher.

The results of determinations of some physical properties of glassy and crystallized samples are given in Table 6, II.

The glass transition and dilatometric softening temperatures of all the glasses increase with nitrogen content, but not proportionally.

The dilatometric softening temperature was over 1000°C for all the crystallized samples.

The thermal expansion coefficient of the glasses decreases with nitrogen content. The expansion coefficient for the crystallized Samples 3, 3.1 and 3.2 is lower than for the corresponding glass samples and also decrease when nitrogen is introduced.

However, for Samples 4.1 and 4.2, this coefficient is increased by crystallization as well by increasing of nitrogen content. This unexpected result might be due to crystobalite, the presence of which could not be clearly established with certitude by XRD because its characteristic lines overlap to some extent with those of cordierite and rutile. This increase in thermal expansion coefficient with increase in nitrogen content, suggests the possibility that its presence in Samples 4.1 and 4.2 favours crystallization of crystobalite.

Determination of microhardness was affected in two cases (marked with asterisc in Table 6,II) by formation of cracks around the identations and in one case by the existence of zones with markedly different average microhardness values (601 and 841 kg/mm^2, respectively).

Within each of the two glass groups, nitrogen presence manifests itself by increasing microhardness, this increase being higher, the higher the nitrogen content. This trend corresponds well with the incorporation of nitrogen into the glasses, where bridging oxygens are remplaces by N_2^{3+} /22/.

The same regularity, although less rigorous, is seen also for crystallized samples.

Conclusions.

Incorporation of nitrogen induces a reduction in thermal expansion of the glasses as well as of the corresponding crystallized samples, except glass-ceramics with TiO_2, for which variation in the opposite direction occured, probably due to crystobalite formation.

The microhardness of the glasses and of the corresponding crystallized samples increases with nitrogen content, a single unimportant deviation being noted.

On the whole, microhardness values are high in agreement with the data from the literature.

The main crystalline phase in all the heat treated samples was cordierite. Along with it, Beta-spodumene was identified in samples without TiO_2, while rutile and crystobalite was identified in samples with TiO_2.

Nitrogen favours the crystallization of crystobalite which is inferred from its absence from the crystallized parent Glass 4, one the one hand, and from its presence in crystallized samples with nitrogen (Samples 4.1 and 4.2) on the other hand.

Of the two groups of heat treated glasses, only that with TiO_2 shows a typical glass-ceramic structure, which shows that nitrogen does not exert a sufficient nucleating action in the amounts present in these glasses.

However, crystal size is clearly smaller in crystallized samples with nitrogen than in those without nitrogen.

The following results are specially noteworthy :

- microhardness = 978 kg/mm^2 (Glass-ceramic 4.2)
- thermal expansion coefficient (25-600°C) = 18.3 x 10^{-7} (Glass-ceramic 3.2).

/. Compositions in the SiO_2-Al_2O_3-MgO-Li_2O Basic System.

Hinz and Kunz/23/ report obtaining of some glass-ceramics with low thermal expansion, from glasses of the cordierite-spodumene system, studied by Karkhanavala and Hummel/24/. This is not a proper binary system, because of other phases (mullite, corundum, spinel) which appear in the SiO_2-Al_2O_3-MgO system.

The interest in their mechanical properties motivated their incorporation in this study.

A mass of this system was experimented, it composition being indicated in Table 1,III.

Because of the chemical agressiveness of the melt towards alumina crucibles, silica crucibles and nitrogen atmosphere were used. Crucible corrosion was sufficiently so as low to allow the melting and the pouring of the glasses.

The parent glass was melted in air, while the glasses with Si_3N_4 were melted in a nitrogen atmosphere. All three glasses were melted at 1600°C and annealed at 700°C.

In the case of Glass 5.2, nitrogen retention was of 85.7 %. The Pouring behaviour and visual description of the glasses are given in Table 2,III.

Heat treatment temperatures and the appearance of heat treated samples are given in Table 3,III.

The results of XRD indicate the presence of a single crystalline phase, spodumene. It means that all the magnesium remained in the composition of the vitrous phase.

Before etching, the heat treated Glass 5 has an appearance which is mainly glassy (Fig. 11). After etching, sections with rough crystals of size exceeding 20 microns, alternating with fine ones, are seen. Fig. 12 shows such a section with large crystals evidenced by etching.

The sample 5.1 is more finely crystallized (Fig. 13). The largest crystallite size is about 2 microns.

The microstructure of Sample 5.2 is characterized by the presence of a certain amount of vitrous phase, from which fine, long crystals of less than 1 micron are growing (Fig. 14).

The fact that in the absence of a nucleating agent, nitrogen containing glasses show, after heat treatment, a structure which becomes finer with higher nitrogen contents, indicates that in the composition of these glasses nitrogen indeed plays the role of a nucleating agent, as mentioned in the literature/13,14/

The glass transition and dilatometric softening temperatures of the glassy samples increase and the thermal expansion decreases when nitrogen is introduced.

For the crystallized samples, the same variation of the expansion coefficient is seen.

The crystallized samples have a much lower thermal expansion than the corresponding glassy ones.

Microhardness shows the same pattern of variation as that seen for glasses in the SiO_2-Al_2O_3-MgO system, before and after heat treatment. It increases with the nitrogen content and is higher with crystallization.

The influence of nitrogen on microhardness is more marked for the glassy samples than for the crystallized ones.

All the samples have a high microhardness.

Conclusions

Contrary to expectations, the only crystallized phase after heat treatment was spodumene, the magnesium entering only into the vitrous phase.

Unlike the previously studied cases nitrogen exerts a clear nucleating action within these glasses, contributing to the existence of crystals smaller than 1 micron.

The change in thermal properties due to nitrogen and due to the transition from vitrous to cristalline state were the same as those in the SiO_2-Al_2O_3-MgO system.

The noteworthy properties of Sample 5.2 are :

- microhardness = 974 kg/mm^2.
- thermal expansion coefficient (25-600°C) of 16.0×10^{-7}.

8. Compositions in the SiO_2-Al_2O_3-CaO Basic System.

Glasses of this system were prepared and studied because of their considerable nitrogen dissolution capability on the one hand and their low melting temperature on the other hand /15/.

The parent Glasses 6 and 7 have the same composition, except for the TiO_2, which was introduced into the latter as nucleating agent.

In Ref. /15/ Loehman shows that Si_3N_4 solubility increases when the SiO_2 content decreases.

The parent Glass 8, with a very low SiO_2 content (13.71 %) is an inverted glass which has a fragmented lattice because of the high modifier cation content.

The melting temperature of the glasses was of 1540-1550^{o}C. Only Glasses 7.1 and 8.1 were melted at 1570^{o}C.

Observing the degree of corrosion of the crucibles in a series of preliminary meltings, silica crucibles were chosen for Glasses 6, 6.1 and 7.1, and alumina crucibles were used for the others.

The melting atmospheres are indicated in Table 1.IV.

The annealing temperature was of 600^{o}C.

Pouring behaviour and visual description of the glasses are given in Table 2.IV.

Heat treatment temperatures and the appearance of the crystallized samples are shown in Table 3, IV.

The XRD diagrams of Samples 6 and 6.1 are characteristic for a non crystalline material, even after heat treatment, at temperatures near the deformation starting temperature i.e. 950^{o}C.

The identified crystalline phases in the other heat treated glasses are shown in Table 4, IV. The XRD diagrams of the crystallized pairs of samples 7 and 7.1 and 8 and 8.1 are practically identical. But there is a marked difference between these two pairs of glasses in the evolution of crystallization and phase composition.

While the DTA curves corresponding to Glasses 7 and 7.1 had a uniformly ascending shape above 800^{o}C, without any marked peak (below 1000^{o}C), these of the Glasses 8 and 8.1 (inverted glasses) had a strong exothermic peak between 860 - 920^{o}C. (see Fig. 22).

In the case of Sample 7, the highest amount of crystalline phase may be calculated assuming that all TiO_2 is crystallized as sphene and neglecting, for time being, the small amount of crystobalite which was detected. The calculations show that this sample contains maximum about 29 wt % crystalline phase in a matrix (with the composition : 17.12% CaO, 18.34% Al_2O_3, 64.54% SiO_2) from which anorthite should have been expected to crystallize.

In the case of Sample 8, assumming that gehlenite crystallized completely, a maximum amount of about 63% crystalline phase is calculated. The residual glass has the composition : 14.67 % CaO, 53.27 % Al_2O_3, 32.06 % TiO_2.

The SEM micrographs of Samples 6 and 6.1 (without TiO_2) from Figs. 15 and 16 show no crystallization in the inner part, and only a thin crystallized external layer is present, which agrees with the results of XRD.

Figs. 17 and 18 show the prevailing glassy nature of the microstructure of Samples 7 and 7.1. In Samples 8 and 8.1 (Figs.19 and 20) a much larger amount of crystalline phase is seen. This confirms the assumptions made before and might offer an explanation for the way microhardness varies when the samples crystallize. The size of the crystals varies in all cases from less than 1 micron to 5-6 microns.

No clear cut difference in microstructure is seen between samples with and without nitrogen.

Comparing the microstructure of samples containing TiO_2 with that of samples without nucleating agent, it is seen that, as expected, the former show a higher degree of crystallization.

Within each pair of glasses (parent glass and glass with nitrogen) the glass transition and dilatometric softening temperatures increase while the thermal expansion coefficient decreases when nitrogen is introduced. An exception is Glass 8.1, for which thermal expansion is slightly higher than for Glass 8 (see Table 6,IV).

For crystallized samples, the same regularity (including the above mentionec exception) is seen.

It is also found that, in comparison with the glassy samples, the crystallized ones have a smaller thermal expansion.

Microhardness increases when nitrogen is introduced into the parent glass and also with the transition from the glassy to the crystalline state.

For Glasses 7 and 7.1 a deviation from this trend is seen, i.e.microhardness is lower for the crystallized samples than for the glassy ones.

The explanation may be looked for in their phase composition. As shown above, in the crystallized Samples 7 and 7.1, there is at most 29 % crystalline phase (especially sphene and little crystobalite). It seens that this amount is insufficient to reinforce and thus strengthen the structure of the crystallized material, and to the contrary, the crystals constitute weakening inhomogenities.

For samples 8 and 8.1, the ration of crystalline phase is more than twice as large (up to 63%), possibly leading to a continuous structure which causes the high microhardness.

Conclusions.

- Nitrogen incorporation does not influence the microstructure of crystallized samples. However, as expected, samples with TiO_2 content, show a more advanced crystallization.
- All glasses and heat treated samples of this series have a high thermal expansion coefficient.
- Microhardness increases with nitrogen incorporation for glassy as well for heat treated samples. The latter have, with the above mentioned deviation, a higher microhardness than before heat treatment.

The microhardness values are generally higher than those obtained for materials in the preceding systems.

The highest obtained values are :

1540 kg/mm^2 for sample 7.1
1384 kg/mm^2 for sample 6.1

both with nitrogen content.

9. Compositions in the SiO_2-Al_2O_3-CaO-MgO Basic System.

The composition of the parent glass 9 is close to that of Glass 6 of the SiO_2-Al_2O_3-CaO system and corresponds to the quaternary euthectique of the SiO_2-CaO.SiO_2-CaO.Al_2O_3.2SiO_2-CaO.MgO.2SiO_2 subsystem, having a liquidus temperature of 1160°C/26/.

Glasses 9 and 9.1 were melted in silica crucibles in unprotected atmosphere, at 1550°C. The annealing temperature was 600°C.

Batch composition, pouring behaviour and heat treatment temperatures (and aspect of treated samples) are indicated in Tables 1,2 and 3.

The XRD diagrams of Samples 9 and 9.1 indicate the absence of crystalline phases, even after heat treatment at temperatures close to the deformation temperature.

The SEM micrograph of Fig.21 shows an appearance entirely similar to that of heat treated Samples 6 and 6.1 of Figs. 15 and 16. Samples 9 and 9.1 are glassy and only a thin crystallized external layer is present, which agrees with the XRD data, as well as with the findings by visual examination.

Thermal characteristics show only a small variation with nitrogen incorporation (see Table 6.V). The dilatometric softening temperature is higher, and the thermal expansion coefficient is practically unchanged after heat treatment.

Microhardness measured before heat treatment increases when nitrogen is incorporated. After treatment, large cracks which affected the precision of the measurements, were seen around the identations.

As compared to materials of the preceding system, materials in the present system have similar thermal expansion coefficients and generally, a lower microhardness.

10. Final Conclusions.

- Nitrogen incorporation leads in all cases to increased melt viscosity.
- Significant changes in the phase composition of the crystallized samples were not seen within the limits of the achieved nitrogen concentrations. Only in two cases, secondary phases which are absent in crystallized parent glasses appear in crystallized samples with nitrogen content (eucryptite and crystobalite, respectively).

  Refractory crystallized phases with nitrogen, like nitrogen-mullite, silicon nitride or silicon oxynitride were not identified.

  This seems to be related to the relatively low nitrogen content on one hand, and to the high content of modifying oxides, on the other.

  Although in the literature there are hints to the possibility that nitrogen could enter the silicate crystal structure, the parallelism in property change of glassy and crystallized samples allows to conjecture that, at least for low contents, nitrogen remains, also after crystallization, in the composition of the residual glass phase.
- Nitrogen exerts a clear nucleating action only in the studied glasses of the SiO_2-Al_2O_3-MgO-Li_2O system.

  Unlike the parent glass, samples with nitrogen show, after heat treatment, the characteristic appearance of glass-ceramics with crystals smaller than 1 micron.

  The possibility should not be excluded that, in higher concentrations, nitrogen would act as a nucleator also in glasses of other systems, as indicated by Chyung and Wusirika, previously quoted.
- Melts obtained in air were generally more fluid and gave, after cooling, glasses of lighter colour than melts obtained in nitrogen atmosphere. Moreover, the change of the various properties after introduction of Si_3N_4 was generally weaker than for melting in nitrogen atmosphere. These findings agree with the data concerning the nitrogen content determined by chemical analysis.

  Nitrogen retention in glasses melted in nitrogen atmosphere (below 1600°C) was 79.4 to 90.7 % , compared to 61.7 to 74.2 % determined for glasses melted in air (with the crucible covered).

- When nitrogen was incorporated into the glass composition, glass transition and dilatometric softening temperatures increases while the thermal expansion coefficient decreases for glassy as well as for crystallized samples.

  In the only case when a substantial increase of the thermal expansion coefficient occurs after nitrogen incorporation, the cause was crystobalite formation.

  The glassy samples have a medium or high thermal expansion. Thermal expansion for crystallized samples are generally lower. The crystallized samples with the lowest thermal expansion coefficient ($\alpha = 8.7x10^{-7} - 16.0x10^{-7}$) were these of the systems with lithium, which contain eucryptite and cordierite, respectively.
- Microhardness increases with incorporation of nitrogen for glassy as well as for crystallized samples, except for the cases when the existence of cracks around identations was noted.

  Comparison of microhardness of samples from various systems shows that it is the highest for samples in the SiO_2-Al_2O_3-CaO basic system, seven of them showing values above 1000 kg/mm^2.

The results show that, even in relatively low proportions, nitrogen causes a considerable change in physical properties of glasses and corresponding glass-ceramics, especially in microhardness.

Some of the studied materials have interesting technical properties.

Their lower melting temperature together with the possibility of using conventional oxide crucibles represent important advantages in their production.

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Fig. 1 Crystallized Sample 1.

Fig.2 Crystallized Sample 1.2

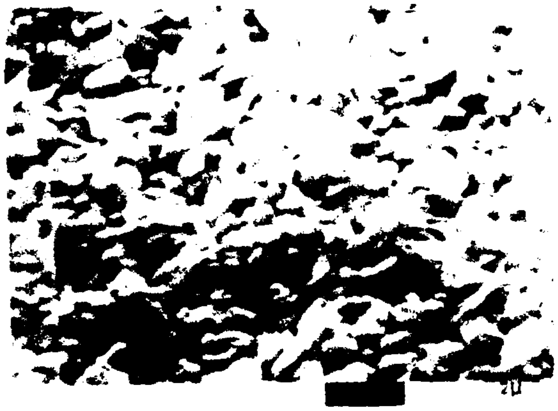

Fig. 3 Crystallized Sample 2

Fig. 4 Crystallized Sample 2.1

Fig. 5 Crystallized Sample 3.1,
crystallized sector

Fig. 6 Crystallized Sample 3.1,
vitreous sector

Fig. 7 Nucleated Sample 4

Fig. 8 Heat treated Sample 4

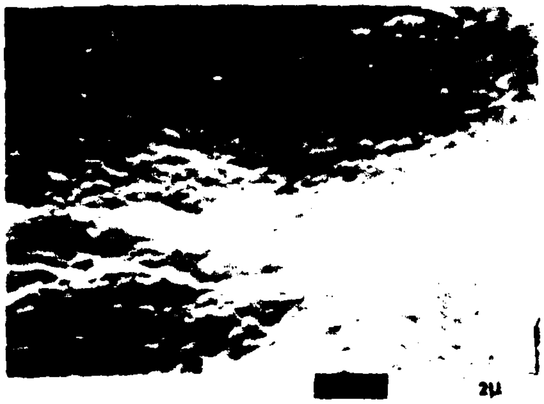

Fig. 9 Heat treated Sample 4.1

Fig. 10 Crystallized Sample 4.2

Fig. 11 Crystallized Sample 5 before etching.

Fig. 12 Crystallized Sample 5 after etching.

Fig. 13 Crystallized Sample 5.1

Fig. 14 Crystallized Sample 5.2

Fig. 15 Heat treated Sample 6

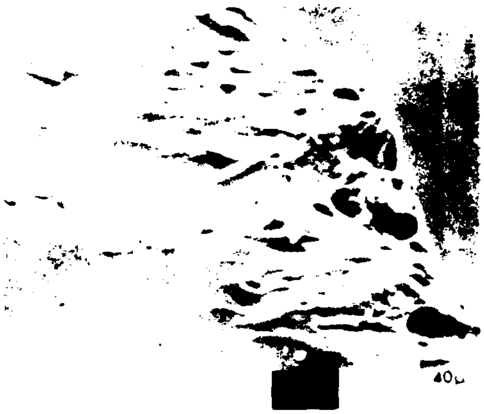

Fig. 16 Heat treated Sample 6.1

Fig. 17 Crystallized Sample 7

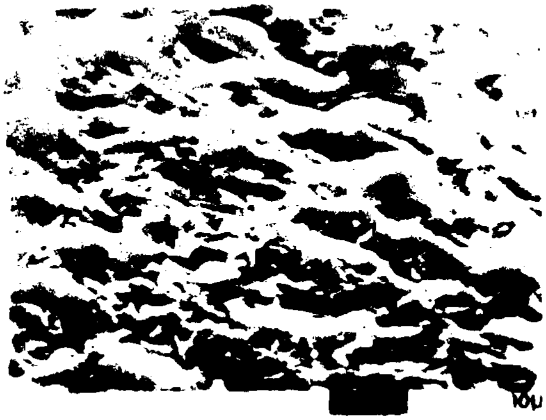

Fig. 18 Crystallized Sample 7.1

Fig. 19 Crystallized Sample 8

Fig. 20 Crystallized Sample 8.1

Fig. 21 Heat treated Sample 9.1

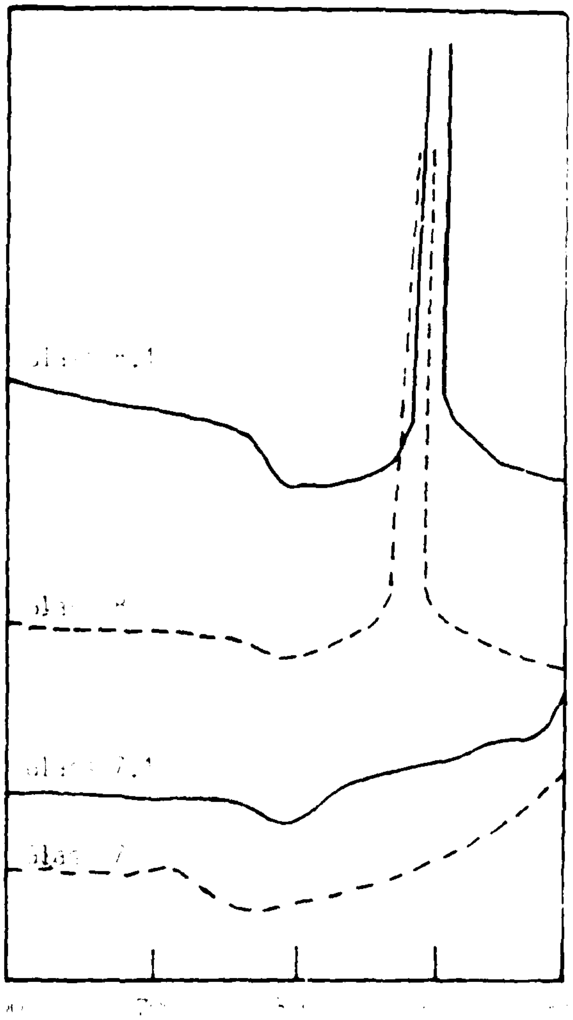

Fig. 22 DTA curves of Samples 7, 7.1, 8, 8.1.

Table 1. Batch Composition*

Batch No.	Wt. %								Melting atmosphere
	SiO_2	Al_2O_3	Li_2O	CaO	MgO	TiO_2	Si_3N_4	LiF	
1	2	3	4	5	6	7	8	9	10
I. BASIC SYSTEM - SiO_2 - Al_2O_3 - Li_2O									
1	75.43	8.93	15.64	-	-	-	-	-	Air
1.1	71.66	8.48	14.86	-	-	-	5.00	-	Nitrogen
1.2	68.25	8.08	14.15	-	-	-	9.52	-	Nitrogen
2	50.71	34.43	10.10	-	-	4.76	-	-	Air
2.1	39.58	35.40	10.37	-	-	4.89	9.76	-	Nitrogen
II. BASIC SYSTEM SiO_2 - Al_2O_3 - MgO									
3	51.76	32.63	-	-	12.61	-	-	3.00	Air
3.1	49.09	30.95	-	-	11.96	-	5.00	3.00	Air
3.2	46.42	29.27	-	-	11.31	-	10.00	3.00	Air
4	46.83	29.83	-	-	11.11	12.23	-	-	Air
4.1	44.49	28.34	-	-	10.55	11.62	5.00	-	Nitrogen
4.2	42.15	26.85	-	-	10.00	11.00	10.00	-	Nitrogen
III. BASIC SYSTEM SiO_2 - Al_2O_3 - MgO - Li_2O									
5	57.50	27.00	4.50	-	8.00	-	-	3.00	Air
5.1	54.54	25.60	4.27	-	7.59	-	5.00	3.00	Nitrogen
5.2	51.57	24.21	4.04	-	7.18	-	10.00	3.00	Nitrogen
IV. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO									
6	62.00	14.70	-	23.30	-	-	-	-	Air
6.1	52.86	15.09	-	23.91	-	-	8.14	-	Air
7	54.56	12.94	-	20.50	-	12.00	-	-	Air
7.1	45.41	13.02	-	21.21	-	12.23	8.13	-	Nitrogen
8	13.71	43.21	-	31.08	-	12.00	-	-	Air
8.1	3.97	44.18	-	31.77	-	12.26	7.82	-	Nitrogen

* The designations of the batches in this Final Report are different from those in the interim reports. The corresponding designations are given in Table 7.

Table 1. Batch Composition (Continued)

Batch No.	Wt. %								Melting atmosphere
	SiO_2	Al_2O_3	Li_2O	CaO	MgO	TiO_2	Si_3N_4	LiF	
1	2	3	4	5	6	7	8	9	10
				V. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO - MgO					
9	59.50	14.20	-	23.80	2.50	-	-	-	Air
9.1	50.35	14.64	-	24.18	2.47	-	8.36	-	Air

Table 2. Pouring Behaviour and Visual Description of Glasses

Glass	Pouring behaviour	External appearance
I. BASIC SYSTEM SiO_2 - Al_2O_3 - Li_2O.		
1	Fluid. Well pourable.	Colorless. Transparent Homogeneous.
1.1	More viscous. Well/satisfactorily pourable.	Grey. Transparent. Homogeneous.
1.2	Viscous. Satisfactorily pourable.	Dark grey. Translucent. Few gas bubbles.
2	Fluid. Well pourable.	Light yellow. Transparent. Homog.
2.1	More viscous. Well/satisfactorily pourable.	Black. Opaque. Transparent in thin layer. Homogeneous.
II. BASIC SYSTEM SiO_2 - Al_2O_3 - MgO.		
3	Well/satisfact. pourable.	Colorless. Transparent. Homog.
3.1	Idem.	Idem.
3.2	Viscous. Satisfactorily pourable.	Grey. Transparent. Some superficial opaque bands.
4	Fluid. Well pourable	Yellow. Transparent. Homogeneous.
4.1	Idem.	Black Opaque. Transparent in thin layer. Homogeneous.
4.2	Idem.	Idem.
III. BASIC SYSTEM SiO_2- Al_2O_5 - MgO - Li_2O.		
5	Fluid. Well pourable	Colorless Transparent. Homogeneous.
5.1	Fluid. Well pourable	Grey. Transp. in thin layer. Translucent in thick layer
5.2	Viscous - Satisf. pourable	Dark grey-brown. Opaque. Transp. in thin layer. Some thin grey layers on surface.

Table 2. (Continued)

Glass	Pouring behaviour	External appearance
	IV. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO	
6	Fluid. Well pourable.	Colorless. Transp. Few gas bubbles.
6.1	More viscous. Well/satisfactorily pourable.	Grey. Transparent. Few gas bubbles.
7	Fluid. Well pourable.	Light yellow. Transparent. Some few gas bubbles.
7.1	Well/satisfactorily pourable.	Black. Opaque. Dark grey and transparent in thin layer. Few gas bubbles.
8	Extreme fluid. Well pourable.	Light yellow-green. Transparent. Few gas bubbles.
8.1	Fluid. Well pourable.	Black. Opaque. Dark grey and transp. in thin layer.Homogeneous.
	V. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO - MgO.	
9	Fluid. Well pourable.	Colorless. Transp. Homogeneous.
9.1	Viscous. Satisfact. pourable	Light grey. Transparent. Few gas bubbles.

Table 3. Treatment Temperatures and Aspect of Samples

Glass No.	Treatment temperatures		Aspect of the samples after heat treatment.
	for nucl., °C	for cryst. °C	
1	2	3	4
I. BASIC SYSTEM SiO_2 - Al_2O_3 - Li_2O.			
1	550	-	Unchanged.
	550	640	Slightly pink, nearly opaque. H.Fr.S *
	550	800	White, slightly pink. Opaque. H.Fr.S.
	550	900	White. Opaque. H.Fr.S.
1.1	550	-	Unchanged.
	550	625	Light blue. Opaque. H.Fr. S.
	550	800	Dark blue. Opaque. H. Fr. S.
	550	900	Lighter blue than for 800°C. Opaque.H.Fr.S. Very thin grey external layer.
1.2	550	-	Unchanged.
	550	640	Grey. Opaque. H. Fr. S.
	550	720	The same as for 640°C.
	550	800	Grey blue. Alternating blue and white grey layers are seen in the fracture.
	550	900	The same as for 800°C.
	550	950	White, loosely adhering layer at the surface. Fracture surface like above.
2	680	-	Unchanged.
	680	950	Light yellow. Lustrous. H. Fr. S.
	680	1000	White, slightly yellow. Opaque. Slightly lustrous. H. Fr. S.
2.1	680	-	Unchanged.
	680	950	Green yellow. Opaque. Lustrous. Stratified fracture surface.
	680	1000	Green yellow. Opaque. Slightly lustrous. H. Fr. S.

* Homogeneous fracture surface.

Table 3. (Continued)

1	2	3	4
			II. BASIC SYSTEM SiO_2 - Al_2O_3 - MgO.
3	800	-	Unchanged.
	800	1200	White. Slightly lustrous. Opaque. H.Fr.S.*
3.1	800	-	Light grey. Transp.
	800	1200	Light grey. Opaque. Slightly lustrous. H.Fr.S.
3.2	800	-	Grey, Translucent/transp.
	800	1200	Grey, with thin white bands on surface. Opaque. Slightly lustrous. Non H.Fr. S.
4	800	-	Yellow - slightly brown. Transp.
	800	1200	White. Opaque. Slightly lustrous. H.Fr.S.
4.1	800	-	Unchanged.
	800	1200	White. Opaque. Non lustrous. Slightly blue fracture surface.
4.2	800	-	Unchanged.
	800	1200	Grey-blue. Slightly lustrous. Opaque. H.Fr.S.
			III. BASIC SYSTEM SiO_2 - Al_2O_3 - MgO - Li_2O.
5	700	-	Unchanged.
	-	1000	White. Opaque. Lustrous. H. Fr. S.
5.1	700	-	Dark grey. Transp. in thin layer.
	-	1000	Grey-blue. Opaque. Slightly lustrous.
	-	-	Stratified fracture surface.xx
5.2	700	-	Dark grey. Transp. in thin layer.
	-	1000	Grey-blue. Opaque. Thin white layer on surface. Slightly lustrous. Strat. Fr. Sxx

* Homogeneous fracture surface.

xx The stratifications visible originate from the pouring stage.

Table 3. (Continued)

1	2	3	4
			IV. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO.
6	750	-	Unchanged.
	750	900	Transparent. Colorless.
	750	950	External translucent crystal. white layer. Glassy fr. surface. Beginning of deformation.
6.1	770	-	Unchanged.
	770	900	External translucent crystal. light-grey layer. Glassy grey fr. s.
	770	950	Idem. Beginning of deformation.
7	800	-	Unchanged.
	800	1000	External: thin, yellowish, opaque, glassy layer. Fracture : glassy, yellowish, homogenous.
	800	1100	Ext. : as at 1000°C. Fr. : white, opaque, weak lustre. homogeneous.
	800	1150	Ext. : white, very slightly yellowish, weak lustre. Fr. : as at 1100°C.
	800	1200	Beginning of deformation. Rounding of the edges.
7.1	820	-	Unchanged.
	820	1000	Ext. : thin, light blue, slightly glassy layer. Fr. : blue-grey, opaque.
	820	1100	Ext. : white-yellowish, slightly glassy Fr. : blue, slightly glassy core.
	820	1150	Ext. : white-yellowish, lustreless. Fr. : white, opaque, lustreless, homogenous
	820	1200	Beginning of deformation. Rounding of the edges.

Table 3. (Continued)

1	2	3	4
8	820	-	Unchanged.
	820	1000	Ext. : white, slightly glassy. Fr. : white, opaque, slightly glassy, homogeneous.
	820	1100	Ext. : slightly yellow, slightly glassy. Fr. : as at 1000°C.
	820	1200	Ext. : yellow, lustreless. Fr. : white, opaque, homogeneous.
	820	1250	Ext. : as at 1200°C. Fr. : as at 1200°C.
	820	1300	Beginning of deformation. Rounding of the edges.
8.1	830	-	Unchanged
	830	1000	Ext. : white-grey, glassy. Fr. : white-grey, opaque, lustreless, homogeneous.
	830	1100	Ext. : yellowish, slightly glassy. Fr. : as at 1000°C.
	830	1200	Ext. : yellow, lustreless. Fr. : white, opaque, lustreless, homogeneous
	830	1250	Ext. : as at 1200°C. Fr. : as at 1200°C.
	830	1300	Beginning of deformation. Rounding of the edges.
			V. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO - MgO.
9	730	-	Unchanged.
	730	900	External translucent crystal. white layer. Glassy fr. surface.
	730	950	Idem. Beginning of deformation.
	730	-	Transparent, pink-brown.
9.1	730	900	Pink-brown. Translucent. Partially cristallized fr. surface.
	730	950	Idem. Beginning of deformation.

Table 4. Nitrogen Content in Oxynitride Glasses.

Glass No.	N. Wt % Calculated	N. Wt % Analyzed	Nitrogen Retention %	Melting atmosphere
1.2	3.80	3.23	85.0	Nitrogen
2.1	3.34	2.06	61.7	Air
3.2	3.99	2.96	74.2	Air
4.2	3.99	3.50	87.7	Nitrogen
5.2	3.99	3.42	85.7	Nitrogen
6.1	3.25	2.26	69.5	Air
7.1	3.25	2.58	79.4	Nitrogen
8.1	3.12	2.93	90.7	Nitrogen

Table 5. Crystalline Phases in the Heat Treated Glasses.

Sample No.	Heat Treatment temp. °C	Main Phases	Secondary Phases
1	2	3	4
		I. BASIC SYSTEM $SiO_2 - Al_2O_3 - LiO_2$	
1.	900	Lithium metasilicate Spodumene.	Lithium aluminum silicate. $(Li_2O.\ Al_2O_3.6SiO_2)$.
1.1	900	Lithium metasilicate. Spodumene.	Lithium aluminum silicate. Eucryptite (Silica O form).
1.2	900	Lithium metasilicate. Spodumene.	Lithium aluminum silicate. Eucryptite (Silica O form).
2	1000	Beta Eucryptite	Rutile.
2.1	1000	Beta Eucryptite	Rutile.
		II. BASIC SYSTEM $SiO_2 - Al_2O_3 - MgO$	
3	1200	Cordierite	Beta-spodumene.solid sol.
3.1	1200	Cordierite	Beta-spodumene, solid sol.
3.2	1200	Cordierite	Beta-spodumene, solid sol.
4	1200	Cordierite	Rutile
4.1	1200	Cordierite	Rutile. Cristobalite ?
4.2	1200	Cordierite	Rutile. Cristobalite ?
		III. BASIC SYSTEM $SiO_2 - Al_2O_3 - MgO - Li_2O$.	
5	1000	Beta - spodumene	None
5.1	1000	Beta - Spodumene	None
5.2	1000	Beta - Spodumene	None

Table 5. (Continued)

1	2	3	4
IV. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO.			
6	900	None	None
6.1	900	None	None
7	1150	Sphene (Ca Ti SiO_5)	Crystobalite
7.1	1150	Sphene	Crystobalite
8	1250	Gehlenite	None
8.1	1250	Gehlenite	None
V. BASIC SYSTEM SiO_2 - Al_2O_3 - CaO - MaO.			
9	900	None	None
9.1	900	None	None

Table 6. Thermal Expansion Coefficient, Transition and Dilatometric Softening Temperatures and Microhardness.

Sample	Properties						
	Before Heat Treatment				After Heat Treatment		
	Glass Trans. Temp. ^0C	Dilatom. softening point ^0C	Thermal expansion coeff. $^0C^{-1} \times 10^7$	Micro hardness kg/mm^2	Dilat. softening point ^0C	Thermal expansion coeff. $^0C^{-1} \times 10^7$	Micro hardness kg/mm^2
1	2	3	4	5	6	7	8
	I. BASIC SYSTEM $SiO_2 - Al_2O_3 - Li_2O$						
1	495	530	86.4	603	-	73.6	803
1.1	520	550	78.7	609	990	48.2	903
1.2	580	610	70.7	619	>1000	33.9	942
2	630	670	66.1	657	800	8.7	560 *
2.1	635	680	64.3	715	880	8.7	772
	II. BASIC SYSTEM $SiO_2 - Al_2O_3 - MgO$						
3	700	740	42.4	814	>1000	26.4	787
3.1	740	780	37.4	874	>1000	26.7	946 *
3.2	760	790	36.7	601/841*	>1000	18.3	-
4	690	740	40.0	861	>1000	24.0	917
4.1	770	810	35.0	882*	>1000	47.3	913
4.2	780	810	32.0	920	>1000	68.8	978
	III. BASIC SYSTEM $SiO_2 - Al_2O_3 - MgO - Li_2O$						
5	610	680	53.3	720*	-	25.6	964
5.1	630	680	46.7	821	>1000	17.3	892 *
5.2	680	730	45.8	935	>1000	16.0	974

* Cracks around the identations.

Table 6. (Continued)

1	2	3	4	5	6	7	8
	IV. BASIC SYSTEM $SiO_2 - Al_2O_3 - CaO$						
6	695	730	63.5	859	730	62.3	966
6.1	730	770	56.5	844*	760	56.1	1384
7	755	810	58.3	1240	860	51.7	825
7.1	775	810	51.7	1540	930	44.7	1000
8	770	820	66.7	1010	>1000	75.8	1155
8.1	790	830	68.3	1130	>1000	80.7	1270
	V. BASIC SYSTEM $SiO_2 - Al_2O_3 - CaO - MgO$						
9	680	725	65.2	903	725	62.2	-
9.1	680	730	59.1	1071	730	59.5	634*

* Cracks around the identations.

Table 7. The Correlation between the Sample Designations in the Final Technical Report and those in the Former Progress Reports.

Sample designations	
in the Final Technical Report	in the Progress Reports
1	A (First Semi-Ann. Progr. Rep.)
1.1	B (- " -)
1.2	C (- " -)
2	4 (Second Semi-Ann. Progr. Rep)
2.1	41 (- " -)
3	1 (First Annual Progr. Rep.)
3.1	11 (- " -)
3.2	12 (- " -)
4	2 (- " -)
4.1	21 (- " -)
4.2	22 (- " -)
5	3 (- " -)
5.1	31 (- " -)
5.2	32 (- " -)
6	5 (Second Semi-Ann. Prog. Rep.)
6.1	51 (- " -)
7	7 (Second Annual Prog. Rep.)
7.1	71 (- " -)
8	8 (- " -)
8.1	81 (- " -)
9	6 (Second Semi-Ann. Prog. Rep.)
9.1	61 (- " -)

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