

Structural changes in sodium-calcium-silicate glass after adding Si_3N_4

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Structural changes in sodium-calcium-silicate glass after adding Si_3N_4 (silicon nitride) were investigated. The research included the use of the atom radial decomposition functions (RDF) and infrared spectroscopy. The results of RDF analysis and infrared absorptive spectroscopy have revealed the existence of oxygen-silicone tetrahedra. Moreover, the most probable nitrogen location in oxide-nitrogen glass has been confirmed.

Keywords: synthesis of oxide-nitride glasses, absorption spectra in the infrared of oxide-nitride glasses, structural changes in oxide-nitride glasses.

1. Introduction

With the development of modern production technology there increases the interest in new materials of specific properties, including glasses. In the group of special glasses the oxide-nitride glasses occupy an import place and in recent years they have become the object of intensive research.

On account of great structural similarity in short range ordering (the length and the angles of bonds) between Si_3N_4 particles and SiO_4 tetrahedra there exists the possibility to incorporate considerable amounts of nitrogen into melted silicate glass.

The first studies concerning the oxide-nitride glasses were dedicated to the problems of physical and chemical solubility of nitrogen from the gaseous phase [1, 2], however the obtained contents were rather small, not exceeding 1 wt% of nitrogen. It was possible to introduce greater amounts of it into the glass structure by way of synthesis of porous boron-silicate glass in ammonia [3]. A distinct increase of the transformation temperature T_g was then observed.

The effect of chemically incorporated nitrogen on the physico-chemical properties of oxide-nitride glasses was in recent years examined in detail and on a large scale. As a result, it was possible to state that the transformation temperature T_g and viscosity η [3–8] increase while the thermal expansion coefficient decreases [5, 9].

Other physical properties have shown a considerable increase in their values with increasing content of nitrogen in the glass, *e.g.*, microhardness [5, 10], chemical resistance, density.

These investigations provide a chance of interesting technological applications for glasses of this type. The above mentioned investigations have been conducted on glasses of various composition. Although they demonstrate similar tendencies there is no possibility to establish the quantitative dependences between the content of nitrogen and the particular properties and structural changes of the glasses.

Moreover, as it follows from a review of literature [5, 11–18] neither the structure of oxide-nitride glasses nor the way the nitrogen becomes incorporated into the structure of these glasses have been definitely determined. Accordingly, further structural as well as physico-chemical investigations are recommended in order to confirm and to supplement the present results and to extend them by including other systems of silicate glasses in the investigations.

2. Experimental method

In order to describe the structure of the glasses obtained the use has been made of X-ray investigations by the method of radial decomposition function (RDF), and infrared absorption spectroscopy.

2.1. Methods of obtaining oxide-nitride glasses

Basic glasses from the $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system were melted in platinum crucibles in an electric silite furnace, at a temperature of above 1450 °C. The molten glass was poured into a specially prepared steel mould. To release the gases dissolved in the glass the samples were refined and placed in a vacuum furnace where they were melted again at a lowered pressure.

Glass obtained in this way was ground and mixed with precisely determined amount of Si_3N_4 , and subjected to accurate homogenization in a rotary mixer. The samples were rinsed for 48 hrs with purified and dried nitrogen in an incubator constructed especially for this purpose. Batches prepared in this way were placed in graphite crucibles in a tightly closed molybdenum pressure container, designed and constructed especially for this purpose. The pressure containers were placed in an induction furnace, kept at appropriate temperature for a definite time period. The synthesis of oxide-nitride glasses was also carried out in a Tammann furnace, slightly modified for this purpose [19].

Preparation of the glasses for melting in the Tammann furnace was the same as in the case of melting in an induction furnace. Nitrogen was also subjected to purification in a system of washers connected in series, filled with H_2SO_4 , and next additionally dried in a tower with silica gel. It was transported through a special system of corundum joints not only to the heating space of the furnace, but also directly to the synthesized

glass, being in contact with the molten glass on the basis of bubbling. The basic glasses, as it has been mentioned, were melted in an electric furnace, while the grinding and refining of the intermediate product were carried out in an agate mill. Both heating systems of the furnace were additionally equipped with an installation for purifying and saturating with nitrogen the heating space of the furnace as well as the samples. After completing the melting the glasses were cooled to ambient temperature remaining all the time in the furnace in argon atmosphere. Afterwards the glass was taken out from the crucibles for preliminary visual assessment.

2.2. Analysis of the decomposition function of atom pairs

Analysis of the decomposition function of atom pairs was carried out on the basis of spectra of X-ray radiation diffraction $K\alpha Mo$ of the wavelength 0.7107 \AA . The measurements were carried out on SIMENS D 500 diffractometer with K 800 generator. The semiconducting meter Si was used as detector.

The curve of the dispersed radiation density was measured by the step method in the interval of angles $6\text{--}164^\circ$. In the analysis there have been taken into consideration the corrections for polarization, absorption, the background and the incoherent dispersion, obtaining the graphs of the function $F(K)$, illustrating the effect of the interference of dispersed radiation on the particular pairs of atoms. This function was transformed by means of Fourier transform, obtaining the function $G(r)$, connected with the radial decomposition of atomic density, and next the RDF(r) and decomposition function of the atom pairs $P(r)$.

2.3. Infrared absorption spectroscopy

Glasses used in structural investigations by means of infrared absorption spectroscopy were prepared by the standard pastille method in KBr (MIR) and in polyethylene (FIR). The spectra were recorded with a Fourier spectrometer DIGILAB FTS-60 (Bio-Rad) in the range of the wave numbers $100.0\text{--}2000.0 \text{ cm}^{-1}$. All the spectra were made with the resolution power 4 cm^{-1} , at 256 scans.

3. Investigation results and discussion

The parameters of the synthesis of oxide-nitride glasses synthesized in an induction furnace and in Tamman furnace, and the percent contents of nitrogen in the glasses according to Kiejdhal chemical analysis [20] are given in Tabs. 1–3.

3.1. RDF analysis

Analysis of the decomposition function of atom pairs of selected samples (4^* and 8^* – denotation according to Tab. 1) was carried out on the basis of the spectra of X-ray radiation scattering. The reduced radial decomposition function of atoms $G(r)$ (glasses Nos. 4^* and 8^*) is shown in Figs. 1 and 2, and the values of the distance r of

Table 1. Parameters of the synthesis of oxide-nitride glasses and percent contents of nitrogen in the glasses, and the content of nitrogen in glasses according to Kiejdhal chemical analysis [20].

Sample	Furnace type	N [wt%]	Melting temperature [°C]	Melting time [h]
1* (MIR)	Electric resistance	—	1450	6.0
2		1.160	1450	1.0
2		1.435	1500	2.0
3		1.837	1550	2.5
3		1.942	1550	3.5
4		2.020	1450	1.5
4		2.116	1550	2.5
4* (MIR /RDF)	Induction	2.470	1550	3.5
4		2.180	1600	6.0
5		3.460	1450	1.5
5		3.150	1550	2.0
5* (MIR)		3.670	1550	3.5
6		3.960	1450	1.5
6		3.984	1500	2.5
6		4.010	1550	3.0
7		4.080	1450	1.0
7		4.120	1500	2.0
7		4.310	1550	3.0
7		4.300	1550	4.0
8		4.410	1500	1.5
8		4.480	1550	2.0
8* (RDF)		4.486	1600	2.5

*Samples selected for further structural and physico-chemical investigations.

Table 2. Parameters of the synthesis of oxide-nitride glasses and percent contents of nitrogen in glasses according to Kiejdhal chemical analysis.

Sample	Furnace type	N [wt%]	Melting temperature [°C]	Melting time [h]
2		1.690	1450	1.0
2		1.435	1550	2.0
3		1.720	1500	1.5
3		1.748	1500	2.5
3		1.710	1550	3.5
4		2.270	1450	1.5
4		2.370	1550	2.5
4		2.341	1600	3.0
5	Tammann	2.410	1500	1.5
5		2.641	1550	2.5
5		2.650	1550	3.0
6		2.690	1450	1.5
6		2.270	1450	2.0
6		2.030	1550	2.5
7		3.240	1450	1.5
7		3.100	1550	1.5
7		3.000	1550	2.5
8		3.360	1500	1.0
8		3.390	1550	1.5
8		3.210	1550	2.5
9		3.180	1500	1.5
9		2.960	1600	2.5

Table 3. List of samples for infrared spectroscopy investigation. Samples marked with numbers with asterisk have been selected for further structural and physico-chemical investigations.

Sample	Si_3N_4 [mol%]	Synthesis temperature [°C]	Time [h]
1*	—	1450	6.00
2	1	1500	2.00
3	3	1550	3.50
4	5	1450	1.50
4	5	1550	2.50
4*	5	1550	3.50
5	7.5	1550	3.00
5*	7.5	1550	3.50
6	9	1550	3.00
7	10	1450	1.50
7	10	1500	2.00
7	10	1550	1.50
7	10	1550	2.50
7	10	1550	3.00
8	12.5	1600	2.50
9	15	1500	1.50
18*	pure Si_3N_4	—	—

Table 4. Mean interatomic distances.

Sample	N	r_1 [Å]	r_2 [Å]	r_3 [Å]	r_4' [Å]	r_4'' [Å]	r_5 [Å]
4*	1.86	1.503	1.902	2.424	2.669	3.037	3.528
8*	1.39	1.503	1.902	2.362	2.792	3.129	3.528

the particular layers of atoms from the central atom and the coordination numbers are listed in Tab. 4.

The mean interatomic distances determined have been assigned to the following pairs of atoms on the basis of literature data [21]:

- r_1 , Si–O: 1.502 Å, 1.502 Å;
- r_2 , Si–Si (on the assumption that the oxygen-silicon tetrahedra become joined at their edges): 1.902 Å, 1.902 Å;
- r_3 , Na–O or Ca–O: 2.424 Å, 2.362 Å;
- r_4' , O–O: 2.669 Å, 2.792 Å;
- r_4'' , Si–Si (belonging to adjacent oxygen-silicon tetrahedra, built of oxygen ions O^{2-} with the radius $r_0 = 1.41$ Å and silicon ions Si^{4+} with the radius $r_{\text{Si}} = 0.41$ Å): 3.037 Å, 3.129 Å.

The composition of the samples and the values r indicate the existence of oxygen-silicon SiO_4 tetrahedra with a silicon atom in the centre. These tetrahedra form

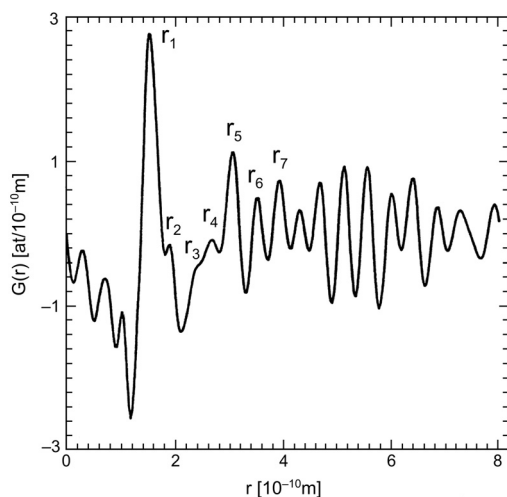


Fig. 1. Reduced radial decomposition function of atoms $G(r)$ of glass No. 4*.

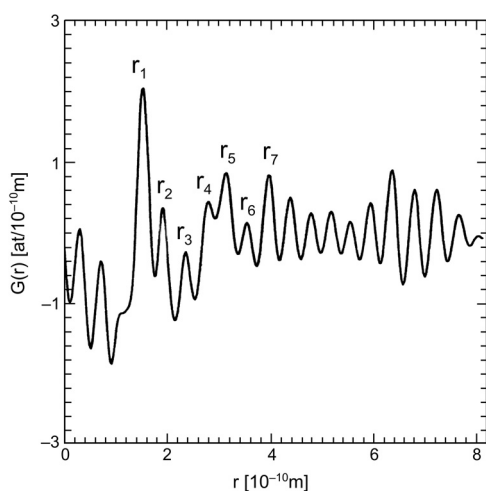


Fig. 2. Reduced radial decomposition function of atoms $G(r)$ of glass No. 8*.

a skeleton in the shape of rings. The small coordination number (about 2) may be an indication that the oxygen-silicon tetrahedra become joined with their nodes in which an oxygen atom is situated with two silicon atoms in the neighbourhood.

The surface areas of peaks of the curve $4\pi r^2 p(r)$ in the case of a polyatomic material correspond to the coordination numbers, *i.e.*, the number of neighbours occurring at a given distance. In case of manyatomic material, these numbers are only of a comparable character. If the atomic composition is not changed, they are proportional to the number of the distances of atoms occurring in the structural unit.

On the graphs of the radial distribution function of atoms it is observed as changes in the distribution of atoms in subsequent layers, defined by the distances r_3 , r_4' and r_4'' . Within SiO_4 tetrahedra, defined by the values of distances r_1 and r_2 , no changes are visible, which is a good evidence that the basic and the only element forming the structural framework is the silicon-oxygen tetrahedron SiO_4 .

RDF investigations have not provided a definite answer to the question of what structural changes follow the Si_3N_4 introduction into the glasses of SiO_2 -CaO- Na_2O system and in what way the nitrogen becomes located in the structure of the glasses.

3.2. Absorption spectra in infrared

The results of investigations with the application of Fourier spectroscopy in the medium and far-infrared range of glasses with systematically changing content of Si_3N_4 introduced are presented in Fig. 3 in accordance with Tab. 3.

Taking into account the intensity of bands connected with the vibrations of the silicon-nitrogen groups the spectra obtained from the middle infrared (MIR) can be divided into three groups:

– spectra of glasses in which the positions of the bands are very close to those of the bands in the spectrum of the basic glass, and the silicon-nitrogen bands are almost invisible;

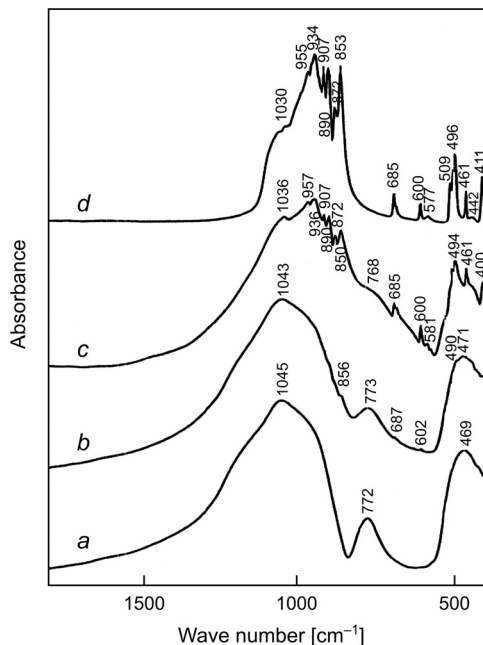


Fig. 3. Spectra of: *a* – basic glass, *b* – glass containing 5 mol% Si_3N_4 , *c* – glass containing 7.5 mol% Si_3N_4 , *d* – pure β - Si_3N_4 .

– spectra of glasses in which the weak bands deriving from the vibrations of silicon-nitrogen bands are observed;

– spectra of glasses with distinctly marked bands, connected with Si_3N_4 .

On the spectra of glasses in similar ranges of the wave numbers there repeatedly occur groups of three bands, connected with the vibrations of the silicon-oxygen framework (obviously, besides $\beta\text{-Si}_3\text{N}_4$). These are the bands situated at: $1050\text{--}1030\text{ cm}^{-1}$, $770\text{--}760\text{ cm}^{-1}$ and $470\text{--}460\text{ cm}^{-1}$.

These bands correspond to vibrations occurring in silicon-oxygen tetrahedra [22, 23]. The band at about 770 cm^{-1} is connected with the bridging vibrations (Si–O–Si) appearing through the combination of two neighbouring tetrahedra. The intensity of this band decreases markedly with an increase of the content of $\text{SiN}_{4/3}$ – on the spectrum of glass containing 5% of $\text{SiN}_{4/3}$ only a kink is visible.

This fact leads to the obvious conclusion that the introduction of silicon nitride causes incorporation of nitrogen atoms into the framework which is connected with the breaking of silicon-oxygen bonds, and thereby with the reduction of the degree of polymerization of the silicon-oxygen framework, so that the position of the band connected with asymmetric tensile vibrations of Si–O at about 1030 cm^{-1} indicates that the degree of the framework polymerization is lower than in the case of skeleton structures (*i.e.*, when T:O = 1:2), since, *e.g.*, in the spectrum of pure silica this band occurs at 1100 cm^{-1} . The third band situated at about 460 cm^{-1} is connected with the deformation (bending) vibrations O–Si–O.

Simultaneously, on the spectra of both oxide-nitride glasses (b) and (c) there appear bands connected with the $\text{SiN}_{4/3}$ introduced. The positions of these bands are almost identical as in the case of pure $\text{SiN}_{4/3}$. The spectra of oxide-nitride glasses have been compared with the spectrum of the starting silicate-calcium-sodium glass and with pure $\beta\text{-Si}_3\text{N}_4$.

A comparison of the spectra of both glasses shows that the intensity of bands connected with the vibrations of silicon-nitrogen groups increases intensively with increasing content of nitride. On the spectrum of glass which contains 5% of $\text{SiN}_{4/3}$ only slight “traces” of bands can be observed, whereas on the spectrum of glass containing 7.5% of $\text{SiN}_{4/3}$ separated maxima are clearly visible. A comparison with $\beta\text{-Si}_3\text{N}_4$ spectrum indicates that bands situated at about: $490\text{--}510\text{ cm}^{-1}$, $600\text{--}680\text{ cm}^{-1}$, $850\text{--}960\text{ cm}^{-1}$, can be regarded as being characteristic of the vibrations of the silicon-nitrogen group.

Assigning the bands to the spectra connected with the vibrations of silicon-nitrogen groups can be used for the description of silicon-oxide bands (to some extent this is justified by the same Si^{4+} coordination both in Si_3N_4 and SiO_2).

The band at about 500 cm^{-1} can thus be assigned to the bending vibrations N–Si–N, whereas the band at 684 cm^{-1} should be associated with the formation of silicon-nitrogen bridges, thus with the joining of silicon-nitrogen tetrahedra. Since the content of $\text{SiN}_{4/3}$ introduced in all the glasses under examination does not exceed 15 mol%, it can be assumed that the joining of $[\text{SiN}_4]^{8-}$ tetrahedra is the evidence of the fluctuation of concentrations of these tetrahedra in the structure of the glasses.

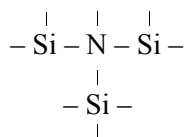
In other words, it can be presumed that there are areas of various types of ordering in the glass, thus the internal structure has a heterogenic character.

The third group of bands in the range $850\text{--}960\text{ cm}^{-1}$ should be associated with silicon-nitrogen asymmetric tensile vibrations, with a great number of bands being connected with various types of “proper” possible bands, *i.e.*, N–Si(N) and N–Si(O), and the “improper” bands, *i.e.* such ones whose presence can be treated as a sort of defects in the glass structure, *i.e.*, N = Si(O), N = Si(N), N \equiv Si(O) and N \equiv Si(N). The position of the bands is connected with the type of anion which is present in the neighbourhood of the bond under consideration.

4. Conclusions

Application of a high pressure molbdenum container in the synthesis process enabled maximum amount of nitrogen equal to 4.486 wt% to be incorporated into the structure of glass from the $SiO_2\text{--}CaO\text{--}Na_2O$ system. In the literature data available this amount does not exceed 4 wt%.

The results of RDF analysis of oxide-nitrite glasses have confirmed the existence of oxygen-silicon tetrahedra SiO_4 . The RDF investigations have not provided a definite answer as to the way the nitrogen becomes situated in the structure of these glasses. The most probable location of nitrogen in oxide-nitrogen glasses has been confirmed according to following model:



References

- [1] MULFINGER H.O., MEYER H., *Über die physikalische und chemische Löslichkeit von Stickstoff in Glasschmelze*, Glastechnische Berichte **36**, 1963, pp. 481–3.
- [2] MULFINGER H.O., *Physical and chemical solubility of nitrogen in glass melts*, Journal of the American Ceramic Society **49**(9), 1966, pp. 462–7.
- [3] ELMER T.H., NORDBERG M.E., *Effect of nitriding on electroanalysis and devitrification of high-silicate glasses*, Journal of the American Ceramic Society **50**(6), 1967, pp. 275–9.
- [4] BOSCHE G., *Konstruktion einer Glasfaserziehangle*, Studentarbeit an Institut für Nichtmetallische Werkstoffe 1987.
- [5] LOEHMAN R.E., *Preparation and properties of yttrium-silicon-aluminium oxynitride glasses*, Journal of the American Ceramic Society **62**(9–10), 1979, pp. 491–4.
- [6] NEUMANN B., KRÖGER C., KUNZ H., *Die Bildungswärmen der Nitride. V. Die Verbrennungswärmen einiger Metalle und Metallnitride*, Zeitschrift für Anorganische Chemie **218**(4), 1934, pp. 379–401.
- [7] DREW R.A., HAMPSHIRE S., JACK K.H., *Nitrogen glasses*, Proceedings of the British Ceramic Society, No. 31, 1981, pp. 119–32.
- [8] JANKOWSKI P.E., RISBUD S.H., *Comparative experimental measurements of viscosity-temperature relations of an oxide and slightly nitrated glasses*, Journal of the American Ceramic Society **65**(2), 1982, pp. C-29–30.
- [9] PIETSCH E. [Ed.], *Gmelins Handbuch der anorganischen Chemie*, No. 4.8 Auflage, Verlag Chemie, 1955, pp. 240–1.

- [10] VERDIER P., PASTUSZAK R., LEMARCHAND V., LANG J., *Nitrogen glasses in the system Ca-Si-Al-O-N. Study of CaO-SiO₂-AlN section*, *Revue de Chimie Minerale* **18**(4), 1981, pp. 361–9.
- [11] KELEN T., MULFINGER H.O., *Mechanismus der chemischen Ausflösung von Stickstoff in Glasschmelzen*, *Glastechnische Berichte* **41**, 1968, pp. 230–42.
- [12] SCHRIMPF C., *Herstellung Stickstoffhaltigen Gläser*, Diplomarbeit am Institut für Steine und Erdem TU Clausthal 1980.
- [13] WUSIRIKA R.R., CHYUNG C.K., *Oxynitride glasses and glass-ceramics*, *Journal of Non-Crystalline Solids* **38-39**, 1980, pp. 39–44.
- [14] JACK K.H., *Sialon and related nitrogen ceramics*, *Journal of Materials Science* **11**(6), 1976, pp. 1135–58.
- [15] JANKOWSKI L., RISBUD S.H., *Synthesis and characterization of Si-Na-B-O-N glass*, *Journal of the American Ceramic Society* **63**(5–6), 1980, pp. 350–2.
- [16] SHILLITO K.R., WILLS R.R., BENNETT R.B., *Silicon metal oxynitride glasses*, *Journal of the American Ceramic Society* **61**(11–12), 1978, p. 537.
- [17] WILDER J., privat communication.
- [18] SCHRIMPF C., *Eingeschaften von Oxinitridgläsern TU Clausthal. Fak Bergbau, Hüttenwes, Maschinenwes, Dr-Ing-Diss* 1982.
- [19] KONDRATOWICZ T., *Synteza szkieł tlenkowo-azotkowych, synteza, aparatura i niektóre właściwości*, *Szkło i Ceramika* **46**, 1995, pp. 21–3 (in Polish).
- [20] PARUS J.K., *Über die Ausführung der Stickstoffbestimmung nach Kiejdhal*, *Glastechnische Berichte* **16**, 1983, p. 374.
- [21] KITAIGORODSKIJ A.J., *Rentgenostrukturyj analiz miekokrystalicznych i amorfnych tie*, Gos. Izd. Tech.-Teoret. Literatury, Moskwa 1952.
- [22] HANDKE M., MOZGAWA W., *Vibrational spectroscopy of the amorphous silicates*, *Vibrational Spectroscopy* **5**(1), 1993, pp. 75–84.
- [23] KONDRATOWICZ T., WASYLAK J., *Nitride-oxide glasses preparation, properties and structure*, *Proceedings of XVII International Congress on Glass, Pekin, Vol. 5*, 1995, pp. 540–5.

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