

Glass-forming region in the Ca–Si–O–N system using CaH₂ as Ca source

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Abstract

The present work explores the glass-forming region in the Ca–Si–O–N system, particularly in the N-rich part of the system. Bulk oxynitride glasses in the Ca–Si–O–N system were prepared by melting mixtures of CaH₂, SiO₂ and Si₃N₄ powders in a nitrogen atmosphere at 1500–1650 °C. The glasses were characterized by X-ray powder diffraction, differential thermal analysis, scanning electron microscopy and transmission electron microscopy. Glass compositions were calculated from analyses obtained by energy dispersive X-ray (EDX) spectroscopy and combustion analysis, for cation and anion compositions, respectively. The glasses were found to be X-ray amorphous and gray to black in color. The glasses retain up to 58 e/o of nitrogen and 42 e/o of calcium. The glass formation depends on reaction kinetics and the precursor used. A strong exothermic reaction is observed at 850–1000 °C, leading to formation of amorphous and crystalline oxynitride phases that melt at high temperatures upon further heating. Glass transition temperatures (T_g) were observed to vary between 798 °C and 1050 °C, and crystallization occurs typically 130 °C above the glass transition temperature. The glass densities vary between 2.79 g/cm³ and 3.25 g/cm³.

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Keywords: Oxynitride glass; Glass-forming region; Calcium content; Nitrogen content; Ca–Si–O–N

1. Introduction

It is difficult to densify Si₃N₄ without an additive, because of the covalent nature of the Si–N bonding. Generally, oxide additives are used to promote the densification via the liquid phase sintering mechanism.^{1–3} CaH₂ has recently been used as an additive for densification of Ca–Si–Al–O–N ceramics.⁴ Furthermore, Ca in metallic form was used as an additive to produce glasses in the Ca–Si–O–N system.⁵ Much of the interest in oxynitride glasses has been stimulated by observation of the large property changes that result from nitrogen incorporation in silicate and aluminosilicate glasses. Compared with their pure oxide counterparts, oxynitride glasses have higher hardness, elastic modulus and fracture toughness.^{6–10} The thermal properties are also affected by the incorporation of nitrogen, resulting in higher glass transition temperatures (T_g) and lower thermal expansion coefficients (α).¹¹

The chemical durability of oxide glasses is appreciably improved by the incorporation of nitrogen, which makes them potential candidates for containment and disposal of high radi-

ation level nuclear waste,¹² and more recently, SiAlON glasses have been cited as interesting host materials for luminescent ions for pigments or LED¹³ or as reinforcement in composites for optical applications.¹⁴ The highly resistive Y–Si–Al–O–N glasses might be of interest as insulators at temperatures where ordinary glasses are too highly conductive.¹⁵

Oxynitride glass formation occurs in a number of M–Si–O–N and M–Si–Al–O–N systems, where M is a modifying cation such as one of the alkali metals (Li, Na, K),^{16–19} the alkaline earths (Mg, Ca, Ba)^{17,19–22} or Y and the rare earth lanthanides.^{16,20,23–27} It has been found that addition of nitrogen in the form of Si₃N₄ promotes glass formation and that the glass-forming regions are relatively small.²⁸ In the case of Mg, glasses comprising 15–28 e/o of Mg and 10–12 e/o of nitrogen have been obtained.^{21,28} Until recently, the amount of nitrogen substituting for oxygen has been rather limited. However, a newly developed synthesis method has enabled the formation of a range of new oxynitride glasses with significantly higher concentrations of nitrogen as well as additives.⁵ In this new synthesis route, the modifier is introduced as a metal, which reacts with nitrogen gas at relatively low temperatures and forms reactive nitride which have not a surface oxide layer. Above ca. 1000 °C, it reacts with SiO₂ (the oxygen source), and then with the usually inert Si₃N₄. A melt containing Si, O, N and the electropositive element is

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then formed, which dissolves remaining SiO_2 and Si_3N_4 . The final melt is then cooled below T_g . Nitrogen contents up to 70 e/o were achieved in the La–Si–O–N system by using this synthesis route.⁵

Glasses with nitrogen contents less than 20 e/o have been synthesized in the Ca–Si–O–N²⁹ and Ca–Si–Al–O–N^{29,30} systems. The properties of the calcium silicon oxynitride glasses are very similar to those of their magnesium counterparts. The Ca–Si–O–N glasses are usually phase separated, with an opaque, milky appearance that closely resembles that of the Mg–Si–O–N glasses.¹⁵ Addition of Al_2O_3 to either system in amounts greater than about 5 wt.% suppresses the phase separation and gives clear, homogeneous glasses.¹⁵

The present work outlines the extent of the glass-forming region of N-rich glass compositions in the Ca–Si–O–N system. Ca metal has good reactivity toward nitrogen gas.³¹ Incorporation of Ca lowers the melt viscosity sufficiently so that Si_3N_4 can dissolve at temperatures at which the melt does not decompose.²⁵ In this study, glasses in the chemical system Ca_3N_2 –CaO– SiO_2 – Si_3N_4 were prepared, and the glass-forming region was investigated.

2. Experimental procedure

Starting compositions for melting experiments were prepared by thoroughly mixing weighed amounts of CaH_2 (98% with Mg < 1%, Alfa Aesar GmbH & Co), CaO (99.9% ChemPur GmbH), Si_3N_4 (ChemPur GmbH), and SiO_2 (99.9%, ABCR GmbH & Co.) powders. Six-gram batches of each composition were ground in a glove box in an argon atmosphere and placed in a niobium crucible, covered with parafilm for avoiding air contact during the transport from the glove box to the furnace. Syntheses were performed in an atmosphere of N_2 gas, serving as nitridation source for Ca. The mixtures were melted at 1500–1650 °C, depending on the composition, using a radio frequency (RF) furnace. The samples were heated up to 650 °C over 15 min and held at this temperature for 30 min to drive off hydrogen completely. The samples were then heated to 1000 °C over 15 min and held at this temperature for 30 min, for complete reaction of calcium with nitrogen, and finally heated up to 1500–1650 °C over 1–2 h, depending on the composition. The melts were cooled by turning off the furnace at the end of the run. CaH_2 powder decomposed at relatively low temperature, ca. 250 °C, to fine-grained and nominally oxygen-free Ca, which was found to be highly reactive towards the nitrogen gas as well as the SiO_2 and Si_3N_4 powders, and a strongly exothermic reaction could be observed at temperatures around 850–1000 °C, with the heat evolution of the reaction depending upon the amount of calcium hydride powder used.

The prepared glasses were examined by X-ray powder diffraction (XRPD), using a Guinier–Hägg camera and $\text{Cu K}\alpha_1$ radiation in order to ascertain the presence or absence of any crystalline phase. Cation compositions were determined by EDX point analysis on polished and carbon-coated surfaces, using a JEOL 820 scanning electron microscope (SEM) equipped with a LINK AN10000 EDX system. Anion contents were determined by combustion analysis (LECO equipment).

The densities were measured according to the Archimedes principle, in distilled water. Measurements were made at 22 ± 1 °C, and assuming a density of 0.998 g/cm³ for water.

Differential thermal analysis (DTA) was carried out in order to determine the glass transition temperature (T_g) and crystallization temperature (T_c). The instrument used was a SETARAM TG-DTA 1600. Crushed pieces of glasses were used, and the measurements were made up to 1400 °C in a flowing argon atmosphere, using Pt cups and a heating rate of 25 °C/min. The onset point of an endothermic shift in the DTA curve was taken as representing T_g , and the onset of an exothermic peak as corresponding to T_c .

3. Results

3.1. The glass-forming region

Forty-nine different compositions were synthesized in order to explore the possible glass-forming region in the Ca–Si–O–N system. The initial compositions are shown in the quaternary diagram given in Fig. 1, where circles represent compositions that form glasses and crosses show those that were found partially crystalline. The compositions that lie below the diagonal line as shown in Fig. 1 were synthesized from the mixtures of SiO_2 – Ca_3N_2 and Si_3N_4 while the compositions that lie above the diagonal line were synthesized from the mixture of SiO_2 –CaO– Ca_3N_2 and Si_3N_4 . The formation of glass was found to be highly dependent on the precursors used and their reaction kinetics. For example, samples with compositions along the diagonal of the quaternary diagram formed glasses (e.g.

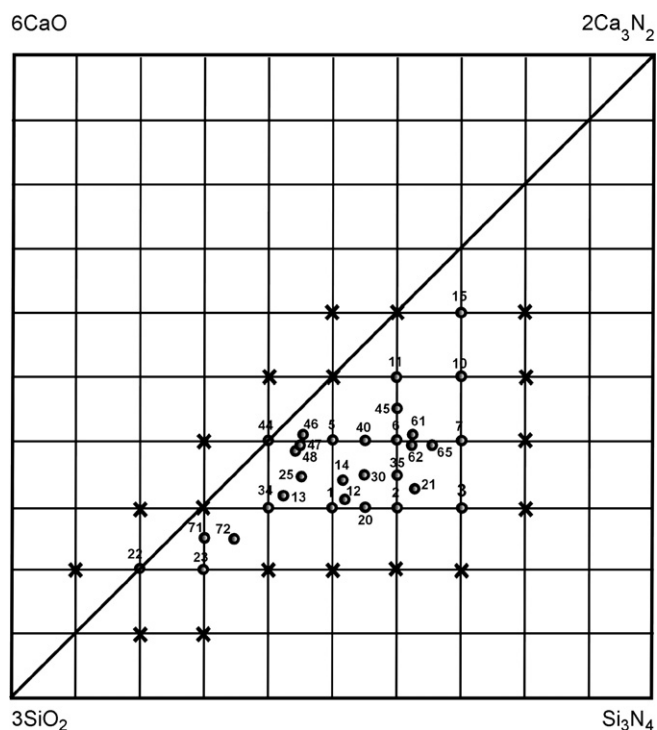


Fig. 1. Before compositions synthesized in the CaO– SiO_2 – Ca_3N_2 – Si_3N_4 system. Circles represent glasses formed, and crosses represent partially crystalline samples.

Table 1

Data for prepared Ca–Si–O–N glasses: Composition of starting mixture, determined glass composition, Ca content in e/o, N content in e/o, X:Si ratio = [O,N]/[Si], glass transition temperature (T_g), crystallization temperature (T_c) and density (ρ)

Glass sample ID	Starting composition	Glass composition	Ca (equiv.%)	N (equiv.%)	X:Si	T_g (°C)	T_c (°C)	Density (gm/cm ³)	Ca silicide (vol.%)
1	Ca _{8.57} Si ₁₀ O _{14.29} N _{9.5}	Ca _{9.94} Si ₁₀ O _{17.73} N _{8.14}	33.2	40.1	2.59	948	1054	3.02	2.05
2	Ca _{8.57} Si ₁₀ O _{11.43} N _{11.43}	Ca _{8.69} Si ₁₀ O _{14.56} N _{9.43}	30.3	49.3	2.40	990	1150	3.05	1.25
3	Ca _{8.57} Si ₁₀ O _{8.57} N _{13.33}	Ca _{9.74} Si ₁₀ O _{13.57} N _{10.78}	32.8	54.4	2.44	1008	1178	3.12	2.45
5	Ca _{13.33} Si ₁₀ O _{16.67} N _{11.11}	Ca _{12.90} Si ₁₀ O _{20.93} N _{7.98}	39.2	36.4	2.89	912	1040	3.02	3.52
6	Ca _{13.33} Si ₁₀ O _{13.33} N _{13.33}	Ca _{11.77} Si ₁₀ O _{16.30} N _{10.31}	37.1	48.7	2.66	967	1050	3.09	1.95
7	Ca _{13.33} Si ₁₀ O ₁₀ N _{11.11}	Ca _{11.04} Si ₁₀ O _{13.21} N _{11.89}	35.6	58.0	2.51	1010	1170	3.24	1.15
10	Ca ₂₀ Si ₁₀ O ₁₂ N _{18.67}	Ca _{13.28} Si ₁₀ O _{17.38} N _{10.58}	39.9	47.8	2.80	955	1120	2.94	0.95
11	Ca ₂₀ Si ₁₀ O ₁₆ N ₁₆	Ca _{12.91} Si ₁₀ O _{20.37} N _{8.36}	39.3	38.1	2.87	935	1045	3.11	1.45
12	Ca ₉ Si ₁₀ O ₁₄ N ₁₀	Ca _{9.3} Si ₁₀ O _{17.8} N _{7.66}	31.8	39.3	2.55	–	–	3.05	–
13	Ca _{9.49} Si ₁₀ O _{17.28} N _{8.16}	Ca _{9.6} Si ₁₀ O _{18.53} N _{7.40}	32.5	37.5	2.59	–	–	3.14	–
14	Ca ₁₀ Si ₁₀ O ₁₂ N ₁₂	Ca _{10.3} Si ₁₀ O _{17.58} N _{8.49}	34.0	42.0	2.61	–	–	3.15	–
15	Ca ₃₀ Si ₁₀ O ₁₅ N _{23.33}	Ca _{10.07} Si ₁₀ O _{12.92} N _{11.40}	33.4	57.0	2.43	1050 ^a	–	3.25	0.80
20	Ca _{8.6} Si ₁₀ O _{22.9} N _{10.5}	Ca _{9.31} Si ₁₀ O _{17.24} N _{8.05}	32.0	40.0	2.53	–	–	3.11	–
21	Ca _{10.5} Si ₁₀ O ₁₁ N ₁₃	Ca _{11.25} Si ₁₀ O _{16.25} N ₁₀	36.0	48.0	2.63	–	–	3.18	4.47
22	Ca ₅ Si ₁₀ O ₂₀ N _{3.33}	Ca _{5.29} Si ₁₀ O _{21.61} N _{2.46}	20.9	14.6	2.41	798	930	2.80	0.93
23	Ca ₅ Si ₁₀ O _{17.5} N ₅	Ca _{4.90} Si ₁₀ O _{20.17} N _{3.15}	19.7	19.0	2.33	830	970	2.81	0.85
25	Ca _{10.8} Si ₁₀ O _{16.9} N _{9.3}	Ca _{10.9} Si ₁₀ O _{21.55} N _{6.24}	35.0	30.0	2.78	–	–	2.97	–
30	Ca _{10.77} Si ₁₀ O _{13.85} N _{11.28}	Ca _{10.74} Si ₁₀ O _{16.08} N _{9.76}	35.0	48.0	2.58	–	–	3.11	–
34	Ca _{8.57} Si ₁₀ O _{17.14} N _{7.62}	Ca _{9.3} Si ₁₀ O _{22.18} N _{4.75}	31.8	24.3	2.69	858	1020	3.02	0.82
35	Ca _{10.77} Si ₁₀ O _{10.77} N _{13.33}	Ca _{10.13} Si ₁₀ O _{15.38} N _{9.84}	33.5	49.0	2.52	–	–	3.20	–
40	Ca _{13.33} Si ₁₀ O ₁₅ N _{12.22}	Ca _{12.32} Si ₁₀ O _{18.52} N _{9.19}	38.2	43.0	2.77	–	–	3.14	–
44	Ca _{13.33} Si ₁₀ O ₂₀ N _{8.89}	Ca _{11.81} Si ₁₀ O _{22.06} N _{6.50}	37.1	30.7	2.86	887	1075	3.13	0.73
45	Ca _{16.36} Si ₁₀ O _{14.55} N _{14.55}	Ca _{12.33} Si ₁₀ O _{18.28} N _{9.38}	38.0	44.0	2.77	–	–	3.17	–
46	Ca _{13.6} Si ₁₀ O _{18.59} N _{10.06}	Ca _{14.65} Si ₁₀ O _{23.12} N _{7.69}	42.0	33.0	3.08	–	–	3.09	–
47	Ca _{12.98} Si ₁₀ O _{18.25} N _{9.86}	Ca _{13.31} Si ₁₀ O _{21.39} N _{7.96}	40.0	36.0	2.94	–	–	3.03	–
48	Ca _{12.48} Si ₁₀ O _{18.05} N _{9.78}	Ca _{12.56} Si ₁₀ O _{21.58} N _{7.32}	38.5	33.7	2.89	–	–	2.98	–
61	Ca _{14.28} Si ₁₀ O _{13.06} N _{14.19}	Ca _{12.71} Si ₁₀ O _{16.81} N _{10.6}	39.0	48.5	2.74	–	–	2.97	4.25
62	Ca _{13.58} Si ₁₀ O _{12.78} N _{13.9}	Ca _{12.46} Si ₁₀ O _{16.29} N _{10.77}	38.5	50.0	2.71	–	–	3.07	3.25
65	Ca _{13.04} Si ₁₀ O _{11.96} N _{14.28}	Ca _{11.56} Si ₁₀ O _{14.87} N _{11.14}	36.5	53.0	2.60	–	–	3.13	–
71	Ca _{6.67} Si ₁₀ O _{18.67} N _{5.33}	Ca _{6.67} Si ₁₀ O _{20.8} N _{3.91}	25.0	22.0	2.47	–	–	2.92	2.85
72	Ca _{6.67} Si ₁₀ O _{17.33} N _{6.22}	Ca _{6.67} Si ₁₀ O _{19.47} N _{4.8}	25.0	27.0	2.43	–	–	2.90	3.05

^a Value not included in graph # 4.

samples 22 and 44 in Table 1) from Ca₃N₂ and SiO₂, but the same compositions failed to form glass when mixing four components, i.e. SiO₂–CaO–Ca₃N₂ and Si₃N₄. Similarly, compositions towards the oxygen rich side of the quaternary diagram did not form glasses when using the present experimental conditions. We believe however, that the glass-forming region extends further towards the left and bottom part of the phase diagram, and that glasses with high oxygen contents can be prepared by alternative routes. In the present work the focus is on determining the glass-forming region for Ca- and N-rich compositions. The starting compositions of the glasses are presented in Fig. 1.

It was found that the synthesis process involves dissociation of some of the components, resulting in a drift of the composition. Elemental analysis of the prepared glasses showed that they had considerably lower contents of nitrogen and calcium than the starting mixtures, and that a loss of these elements occurs at the comparatively high preparation temperatures (1550–1650 °C) used. Si losses were also noticed for some compositions. The determined glass compositions are listed in Table 1. In Fig. 2 the area outlined by a dashed line shows the glass-forming region observed in the present work, while

the solid circle represent the glass-forming region reported by Hampshire et al.²⁹

The glasses obtained in the Ca–Si–O–N system have X:Si [X = O, N] ratios between 2.33 and 3.08, corresponding to high and low average connectivity limits. The concept of connectivity has often been invoked to explain changes in properties of oxynitride glasses and it has been argued that N is probably to a large extent three-coordinated. The X:Si ratios around three for some of the present glasses appears to indicate, however, rather fragmented networks. The densities of the glasses were found to have values ranging from 2.79 g/cm³ to 3.25 g/cm³.

The obtained glasses were homogeneous and were of limited transparency, having colors varying from gray to almost black, optical microscopy and SEM observations showed that some of the glasses contain small amounts of spherical particles of Ca silicide. The size of the spherical particles ranged from less than 0.2 μm to 4 μm and more. The amount of silicide particles was estimated as less than 2 vol.%, but for some samples it was as high as 5 vol.%. The amount showed no clear variation with glass composition. It was observed that increasing the concentration of CaH₂ in the system lowered the glass melting temperature and enhances reaction kinetics.

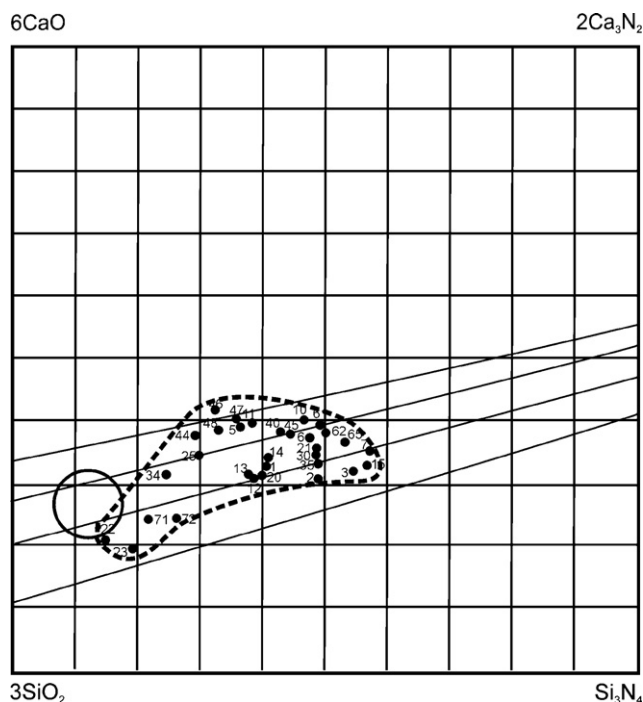


Fig. 2. Glasses obtained in the CaO–SiO₂–Ca₃N₂–Si₃N₄ system. The solid circle envelops previously prepared Ca–Si–O–N glasses.²⁹ The slanting lines show selected constant values for the X:Si ratio = [O,N]/[Si], from 2.25 to 3.00.

3.2. Glass transition and crystallization temperatures

Observed glass transition temperatures, T_g , and crystallization temperatures, T_c , are listed in Table 1 for 13 glasses in the Ca–Si–O–N system. DTA recording for Ca_{5.29}Si₁₀O_{21.61}N_{2.46} glass sample (no. 22 in Table 1) is shown in Fig. 3. The glass transition temperatures range from 790 °C to 1050 °C, and crystallization temperatures from 870 °C to 1220 °C. The average temperature difference between T_g and T_c is approximately 130 °C.

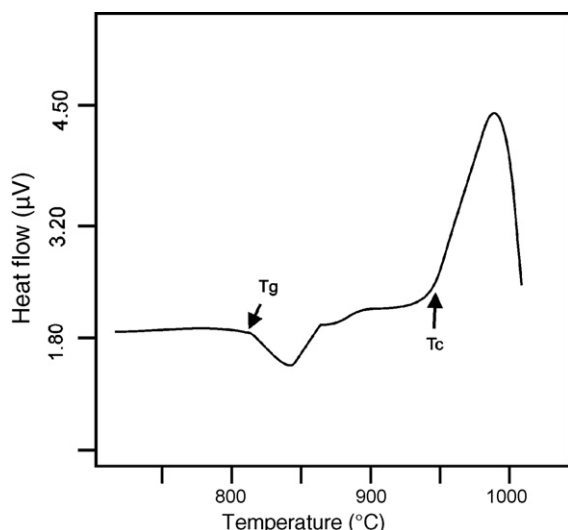


Fig. 3. DTA recording for Ca_{5.29}Si₁₀O_{21.61}N_{2.46} glass sample (no. 22).

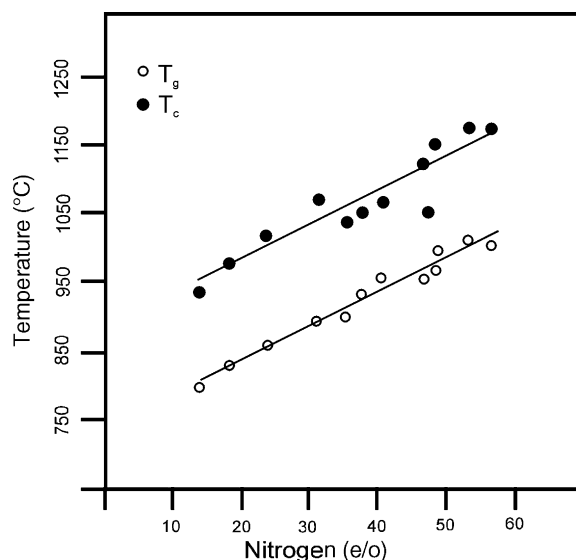


Fig. 4. Glass transition temperature (T_g) and crystallization temperature (T_c) as a function of N content for Ca–Si–O–N glasses.

Fig. 4 shows that there is a significant increase in T_g with increasing nitrogen content. Since the addition of nitrogen content increases the cross-link density in the glass structure, the glass transition temperature is expected to increase as the nitrogen content of the glass increases in the Ca–Si–O–N system. A fit of the data to a linear dependence of T_g on both N and Ca content yielded $T_g = 738(17) + 4.9(3) \cdot [N] - 0.1(6) \cdot [Ca]$. The data thus indicate that the Ca content has less effect on T_g than the N content. The dependence on the Ca content is, however, comparatively more difficult to ascertain due to that the variation in Ca content is for the glasses smaller than the variation in N content.

4. Discussion

The results of the present study demonstrate that Ca–Si–O–N glasses can be obtained in reasonable quantity over a wide composition range in the system, containing up to 58 e/o nitrogen and 42 e/o calcium. Samples with Ca and N contents, respectively higher than 50 e/o and 70 e/o were observed to be partially crystallized. Glass formation depends on the precursors used and their reaction kinetics. The use of calcium hydride as a source of calcium, instead of calcium oxide as additive, has the advantage that calcium functions as a nitrogen source by reacting with the nitrogen atmosphere and thus facilitates the preparation of nitrogen rich compositions. Calcium hydride is more reactive towards SiO₂ and Si₃N₄, and intimate mixtures of intermediate phases are formed upon the exothermic reaction at 850–1000 °C, providing improved reaction kinetics upon further heating.

A comparison of the compositions of the glasses and the starting mixtures shows that primarily Ca, Si and N are lost during the heat treatment. The losses of Si and Ca depend on the starting composition: if it is Ca-rich, then Ca is preferentially lost. It was also observed that the larger the amount of Ca in the starting mixture, the higher will be the loss of Ca in the glass

mixture. Si loss was noticed when the starting composition contained 65–75 e/o of Si. No loss of Ca and Si was noticed from starting composition containing 75–80 e/o Si. Measurement of the nitrogen contents of the glasses by combustion analysis indicated that about 15–30 e/o of the nitrogen initially added was lost upon melting. Nitrogen loss depends on the amount of nitrogen in the starting mixture, melting temperature and holding time. The losses were found to increase with high amount of nitrogen content in the starting mixture, high temperature and, to a less extent with holding time. This might be due to the decomposition reaction proposed by Messier and Deguire,³² whereby Si departs as gaseous SiO. The reaction implies, however, the formation of elemental Si, whereas the glasses contain very small amounts of elemental Si as evidenced by TEM study.

Since an increase in nitrogen content increases the number of Si–N bonds in the glass structure, the glass transition temperature is expected to increase as the nitrogen content of the glass increases. An increase in the glass transition temperature is observed as the amount of nitrogen increase in the Ca–Si–O–N system. A best-fit line through the data in Fig. 4 yields an empirical expression for the glass transition temperature:

$$T_g (^{\circ}\text{C}) = 736 + 4.93 \cdot [\text{N}] \text{ e/o}$$

The T_g values for some of the present Ca–Si–O–N glasses are high in comparison with values reported in the literature for oxynitride glasses. However, values in the range of 1000–1100 °C have been determined for nitrogen-rich La–Si–O–N glasses.³³

5. Conclusions

Homogeneous glasses in the Ca–Si–O–N system containing up to 58 e/o nitrogen and 42 e/o Calcium have been prepared by a novel route, by heat-treating mixtures of CaH₂, SiO₂ and Si₃N₄ powders in a nitrogen atmosphere at 1500–1650 °C. The glass-forming region is found to be quite large, and the formation of glasses strongly depends on the precursors used. A strongly exothermic reaction is observed at 850–1050 °C proportional to the amount of CaH₂ used in the starting composition. The limited transparency and grayish-blue to black color of Ca–Si–O–N glasses are due to the presence of silicides in the glasses. The glasses appeared to lose Ca, Si and N during the melting process. Glass transition temperatures increase with increasing nitrogen content.

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