

Compositional effects on the properties of high nitrogen content alkaline-earth silicon oxynitride glasses, AE = Mg, Ca, Sr, Ba

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Abstract

A series of alkaline-earth element containing high nitrogen content oxynitride glasses (AESiON), with AE = Mg, Ca, Sr, Ba, were prepared in order to investigate the compositional effects on the physical properties of the alkaline-earth element. The physical properties were found to change linearly with the concentration of AE elements. The density of the glasses increases substantially with an increase in the AE atomic mass and slightly with an increase in nitrogen ratio. Ba containing glasses shows the value of density 4.16 g/cm³. Glass transition temperatures are found to be higher for Mg glasses, *ca.* 1020 °C, in comparison with Ba glasses, *ca.* 895 °C. The hardness of Mg containing glasses shows high values, up to 12.2 GPa and decreases for Ca, Sr and Ba containing glasses. Ba, containing glasses shows high values of refractive index in comparison with the Sr, Ca and Mg containing glasses.

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1. Introduction

Silicon oxynitride glasses were first discovered as grain boundary phases in silicon nitride based ceramics. Since the high-temperature behavior of the ceramics is markedly governed by the intergranular glassy phases, having a negative effect on the mechanical properties, studies of the glasses became quite important.^{1–3} Since it is experimentally difficult to investigate directly the properties of grain boundary phases, research on them in bulk form was initiated. Since then, oxynitride glasses have received considerable attention, from both scientific and technological points of view, as it was realized that incorporation of nitrogen into silicate glasses causes profound alterations of mechanical properties such as strength, toughness, elastic modulus, and hardness.^{4–12} It was also found that the thermal properties are also affected, with oxynitride glasses having higher glass transition temperatures (T_g) and lower thermal expansion coefficients (α).¹³ Oxynitride glasses show furthermore the highest refractive indexes ever obtained for silicate based glasses.¹⁴

The way in which the composition of the oxynitride glasses determines their physical properties is of both fundamental interest and of importance for applications. For oxynitride glasses with rare-earth (RE) elements, studies^{15–18} have shown that changes in molar volume (MV), hardness, elastic properties and glass transition temperature (T_g) are controlled by the cation field strength (CFS) of the modifier or an effective CFS in the case of a mixed modifier glass. The oxidation resistance of RE–Si–Al–O–N glasses is, furthermore, found to increase with decreasing radius of the RE ion.¹⁸ It is, however, clear, as shown by, e.g. the study by Becher et al.,¹⁰ that the Young's modulus and microhardness of RE–Si–Al–O–N glasses (RE = La, Nd, Gd, Y, Lu) not only depend on the type of RE element but also on the concentration of the RE and the amount of nitrogen.

Very limited research has been carried out so far in oxynitride glasses with alkaline-earth (AE) elements.^{5,19–25} For AE–Si–Al–O–N glasses¹⁹ with AE = Mg, Ca and Ba the density increases with increasing atomic number of the AE element. A comparison of the results of Homeny and McGarry²⁰ for Mg-sialon glasses and Sakka et al.²¹ for Ca-sialon glasses similarly confirms that Ca-sialon glasses have higher densities than corresponding Mg-sialon glasses. Videau et al.²² found that Mg and Ca oxynitride glasses, with the same amounts of N, have similar T_g values, albeit slightly higher in the case of Mg, whereas

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the corresponding Ba glasses have lower T_g values. However, contrary results were obtained by Drew et al.,²³ who found that Ca glasses exhibit higher T_g and T_c values than corresponding Mg glasses. The microhardness of AE–Si–Al–O–N glasses²² (AE = Mg, Ca, Ba) decreases with increasing atomic number of the AE element. The refractive index²³ of oxynitride AE glasses is found to increase when Mg is replaced by Ca.

Oxynitride glasses have traditionally been synthesized by melting mixtures of glass modifier metal oxides, SiO₂ and Si₃N₄, yielding glasses with nitrogen content up to typically ca. 30 e/o (N content in equivalents; e/o = 3[N]/(3[N] + 2[O]), where [N] and [O] are the atomic concentrations of N and O, respectively). However, the synthesis route recently discovered^{14,26–29} has enabled the preparation of oxynitride glasses with significantly higher concentrations of nitrogen, as well as modifier additives. In this synthesis route, the modifier is introduced as a metal or metal hydride, which reacts with nitrogen gas at relatively low temperatures and forms reactive nitrides with no surface oxide layer. Above ca. 1000 °C, they react with SiO₂ (the oxygen source), and then with the usually inert Si₃N₄. A melt containing Si, O, N, and the electropositive element is then formed, which dissolves remaining SiO₂ and Si₃N₄. The final melt is then cooled below T_g . The oxynitride glasses in AE–Si–O–N systems (where AE is Mg, Ca, Sr and Ba) were prepared by using this novel synthesis method.

The aim of the present work is to gain quantitative knowledge of the factors controlling the properties of oxynitride glasses with different AE modifiers and also effect of nitrogen on the glass properties in different AE–Si–O–N systems. The nominal compositions for all four series in the AE–Si–O–N glasses were chosen identical (cf. Table 1). Four glasses in each series of AE–Si–O–N, having different alkaline earth and nitrogen contents were prepared and then the property variations were discussed with respect to the effect of alkaline earth and nitrogen contents in the glass.

2. Experimental

2.1. Materials specifications and powder mixing

Oxynitride glasses in the alkaline earth silicon oxynitride systems were prepared from mixtures of MgH₂ (95.5% metal basis, Alfa Aesar GmbH & Co), CaH₂ (98% with Mg < 1%, Alfa Aesar GmbH & Co), SrH₂ (95.5% metal basis, Alfa Aesar GmbH & Co), BaH₂ metal (95.5% metal basis, Alfa Aesar GmbH & Co), Si₃N₄ (ChemPur GmbH), and SiO₂ (99.9%, ABCR GmbH & Co) powders. All chemicals were stored in a glove box compartment under Ar atmosphere to avoid exposure to air. The powders were weighed inside the glove box and then pressed into pellets. Six gram of batches for each composition was placed in niobium crucibles, covered with parafilm to avoiding air contact during the transport between the glove box and the furnace.

2.2. Synthesis

Syntheses were performed in an atmosphere of N₂ gas, serving as nitridation source for metal hydride. The mixtures were melted at 1500–1700 °C, depending on the composition, using a radio frequency furnace or a graphite furnace. The samples were heated up to 650 °C during 15 min and held at this temperature for 30 min to drive off hydrogen. The samples were then heated to 1000 °C during 15 min and held at this temperature for 30 min, for a complete reaction of the metals with nitrogen gas, and then finally heated up to 1500–1700 °C during 1–2 h, depending on the composition. The melts were cooled by turning off the furnace at the end of the run. The use of AEH₂ precursor as additive has the advantage that it functions effectively as a nitrogen source, by reacting with the nitrogen atmosphere, and thus facilitates the preparation of nitrogen rich compositions. During heating, a strong exothermic reaction was observed at temperatures 650–1000 °C, associated with a rapid nitrida-

Table 1
Glass designation, composition of starting mixture, determined glass composition, and contents of AE (AE = Mg, Ca, Sr or Ba), Si, O, N in equivalent % (e/o).

Glass ID	Starting composition	Glass composition	Starting composition, equiv.%				Glass composition, equiv.%			
			AE	Si	O	N	AE	Si	O	N
Mg-1	Mg ₅ Si _{10.5} O _{20.5} N _{3.63}	Mg _{3.07} Si ₁₀ O _{18.98} N _{2.46}	19.0	81.0	79.0	21.0	13.3	86.7	83.7	16.3
Mg-2	Mg _{7.6} Si _{10.5} O _{18.5} N _{6.68}	Mg _{4.27} Si ₁₀ O _{17.72} N _{4.32}	26.5	73.5	65.0	35.0	17.6	82.4	73.2	26.8
Mg-3	Mg _{10.1} Si _{10.5} O _{16.5} N _{9.63}	Mg _{5.85} Si ₁₀ O _{15.98} N _{6.31}	33.5	67.5	53.5	46.5	22.6	77.4	62.8	37.2
Mg-4	Mg _{12.4} Si _{10.5} O ₁₅ N _{12.03}	Mg _{7.04} Si ₁₀ O _{15.63} N _{7.46}	37.0	73.0	45.5	54.5	26.0	73.9	58.3	41.7
Ca-1	Ca ₅ Si _{10.5} O _{20.5} N _{3.63}	Ca _{3.41} Si ₁₀ O _{19.75} N _{2.45}	19.0	81.0	79.0	21.0	14.6	85.4	84.3	15.7
Ca-2	Ca _{7.6} Si _{10.5} O _{18.5} N _{6.68}	Ca _{6.52} Si ₁₀ O _{20.02} N _{4.43}	26.5	73.5	65.0	35.0	24.6	75.4	75.1	24.9
Ca-3	Ca _{10.1} Si _{10.5} O _{16.5} N _{9.63}	Ca _{8.03} Si ₁₀ O _{17.92} N _{6.65}	33.5	67.5	53.5	46.5	28.7	71.4	64.2	35.8
Ca-4	Ca _{12.4} Si _{10.5} O ₁₅ N _{12.03}	Ca _{9.14} Si ₁₀ O _{17.37} N _{7.84}	37.0	73.0	45.5	54.5	31.4	68.6	59.6	40.4
Sr-1	Sr ₅ Si _{10.5} O _{20.5} N _{3.63}	Sr _{3.88} Si ₁₀ O _{20.23} N _{2.38}	19.0	81.0	79.0	21.0	16.3	83.8	85.0	15.0
Sr-2	Sr _{7.6} Si _{10.5} O _{18.5} N _{6.68}	Sr _{6.89} Si ₁₀ O _{20.19} N _{4.33}	26.5	73.5	65.0	35.0	25.6	74.4	75.7	24.3
Sr-3	Sr _{10.1} Si _{10.5} O _{16.5} N _{9.63}	Sr _{8.02} Si ₁₀ O _{18.08} N _{6.56}	33.5	67.5	53.5	46.5	28.6	71.4	64.8	35.2
Sr-4	Sr _{12.4} Si _{10.5} O ₁₅ N _{12.03}	Sr _{10.52} Si ₁₀ O _{18.22} N _{8.11}	37.0	73.0	45.5	54.5	34.5	65.5	59.9	40.4
Ba-1	Ba ₅ Si _{10.5} O _{20.5} N _{3.63}	Ba _{4.72} Si ₁₀ O _{21.23} N _{2.34}	19.0	81.0	79.0	21.0	19.1	80.9	85.8	14.2
Ba-2	Ba _{7.6} Si _{10.5} O _{18.5} N _{6.68}	Ba _{7.09} Si ₁₀ O _{20.58} N _{4.32}	26.5	73.5	65.0	35.0	26.2	73.8	76.1	23.9
Ba-3	Ba _{10.1} Si _{10.5} O _{16.5} N _{9.63}	Ba _{8.05} Si ₁₀ O _{19.02} N _{6.26}	33.5	67.5	53.5	46.5	28.7	71.3	66.9	33.1
Ba-4	Ba _{12.4} Si _{10.5} O ₁₅ N _{12.03}	Ba _{11.45} Si ₁₀ O _{19.28} N _{7.99}	37.0	73.0	45.5	54.5	36.4	63.6	61.7	38.3

tion of metal, resulting in the formation of both crystalline and amorphous phases, which then melted upon a further increase of temperature. The temperature at which a melt formed was found to increase with increasing amount of Si₃N₄ and decrease with increasing alkaline earth content. The time for melt formation was also found to decrease with increasing alkaline earth content.

2.3. Glass characterization

2.3.1. X-ray analysis and optical microscopy

The state of the samples was verified by powder X-ray diffraction, using a Panalytical X'pert PRO MPD diffractometer and CuK α ₁ radiation. A light microscope (Olympus PMG3, Japan) was used to observe the surface morphology of the samples and to estimate amounts of present metal silicide impurities.

2.3.2. SEM and TEM analysis

For microstructure examinations, specimens were prepared by hot-mounting them in bakelite, grinding with silicon carbide papers, and polishing with a diamond powder impregnated wheel. The chemical homogeneity of the glasses was examined by back-scattered electron images using a JSM 7000F scanning electron microscope. Cation concentrations were determined by energy dispersive X-ray (EDX) point analysis, 20 on each sample, on polished and carbon-coated surfaces, with a Si detector and a LINK INCA program system. Oxygen and nitrogen contents were determined by combustion analysis using a LECO equipment. For transmission electron microscopy (TEM) observations, the sample was crushed in an agate mortar, dispersed in ethanol and dropped on a carbon microgrid. High-resolution TEM (HRTEM) was performed with a JEOL JEM-3010 microscope operating at 300 kV ($C_s = 0.6$ mm, point resolution 1.7 Å). Images were recorded with a CCD camera (MultiScan model 794, Gatan).

2.3.3. Density, molar volume, and compactness

The densities of the glasses were measured according to the Archimedes principle (ASTM C373-88) in distilled water. Density values were calculated using the expression $\rho = m_d / (m_d - m_w) \cdot \rho_{\text{water}}$, where m_d is the weight of the dry sample, m_w is the weight of the immersed sample and ρ_{water} at 20 °C is 0.9982 g/cm³. Sample weights were between 200 and 400 mg and measured glass densities were reproducible to ± 0.01 g/cm³.

Molar volumes (MV) of the glasses were calculated using the following expression (1), with X_i and M_i being, respectively, the mole fraction and molar mass of element i , respectively, and ρ is the density of the glass.

$$MV = \frac{\sum_i x_i m_i}{\rho} \quad (1)$$

The compactness (C) of the glasses, which is related to the excess volume of the glass, is defined as the ratio between the summed volume of the individual ions and the corresponding volume of

glass. It is calculated using the expression

$$C = \frac{\sum_i x_i V_i N}{MV} \quad (2)$$

with V_i being the ion volume for element i , calculated using the ionic radii given by Shannon,³⁰ and N denoting Avogadro's number.

2.3.4. Cationic field strength (CFS)

In order to reveal the effect of the alkaline-earth ions, the thermal and physical property values have been compared as a function of CFS. The cation field strengths (CFSs) of the modifier ions were calculated as, respectively, 3.858, 1.780, 1.366, 1.050 Å⁻² for Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, using the following expression.

$$CFS = \frac{Z}{r^2} \quad (3)$$

where Z is the valence of the respective alkaline-earth ion and r the Shannon–Prewitt cationic radius,³⁰ for 6-coordinated Mg and 7-coordinated Ca, Sr and Ba.

2.3.5. Differential thermal analysis

Glass transition temperatures (T_g) and crystallization temperatures (T_c) were measured on crushed pieces of glass, using a SETARAM Labsys TG-DTA 1600 instrument. Samples were heated up to 1350 °C in flowing nitrogen in Pt cups, using a heating rate of 25 °C/min. The onset point of an endothermic drift on the DTA curve was taken as representing T_g , and the onset of an exothermic peak as corresponding to T_c . The precision in the T_g and T_c measurement was estimated to be ± 5 °C.

2.3.6. Vickers hardness

The Vickers hardness measurements were carried out on polished samples using a Matsuzawa micro hardness tester Model MXT- α 1, and a Vickers hardness testing machine equipped with a pyramidal diamond indenter under an applied load of 300 g. The indentation dimension for each sample was measured with a light microscope (Olympus PMG3, Japan) under a magnification of 200, and hardness values were calculated in GPa according to Anstis et al.,³¹ using the expression $H_v = (18.42P)/d^2$, where P [N] is the load applied on the indenter and d [μ m] is the average indentation diagonal length. Twelve indentations per specimen were normally recorded and their mean value and standard deviation then calculated.

2.3.7. Refractive index

Since the majority of the present glasses were not transparent, n was estimated by measuring the Brewster angle θ_B on polished glass surfaces, with a laser light source operating at $\lambda = 640$ nm, and using the equation $n = \tan(\theta_B)$. The measurement precision was estimated to be about ± 0.05 , corresponding to an error in $2\theta_B$ of approximately 2°.

3. Results and discussion

3.1. Glass formation

Sixteen glasses (four in each system) having different compositions were synthesized in order to explore the effect of the modifiers and nitrogen contents in the AE–Si–O–N systems. X-ray powder diffraction confirmed the amorphousness of the glasses. The glasses were inspected visually and by optical microscopy at 200 \times magnification, on polished surfaces of each glass, to evaluate their homogeneity and the extent of silicide particles present. The homogeneity was confirmed by back scattered electron SEM images and EDX point analysis. The obtained glasses were homogeneous, with varying colors. The Mg–Si–O–N glasses were pink (light-red) and translucent for low Mg contents and transparent for a high Mg content. The Ca/Sr glasses were opaque black and the variation of color did not change significantly with the amount of Ca/Sr. The Ba containing glasses ranged in appearance from transparent grey to barely translucent black, with the transparency decreasing with Ba content.

Optical microscopy and SEM observations showed that the glasses contained small amounts of spherical particles of silicides, found also in previous studies.^{24,27–29,32} We hold it likely that, during the synthesis, part of the initial Si₃N₄ and SiO₂ is reduced at an early stage to form silicides with the modifier element. At the high synthesis temperatures used, the silicides are molten, which accounts for their spherical particle shape. The reaction mechanism for this reduction is not known, but possibly it involves a direct reaction between AE metal and Si₃N₄ to produce AE_xSi_y + N₂ or AE₂N₃ + Si, with a subsequent reaction of AE and Si. The size of the particles ranged from less than 0.1 μ m to 2 μ m and their amounts were estimated to be less than 2 vol%. The amounts of silicides in the glasses showed no systematic variation with glass composition. The presence of silicides is evidently unwanted and is likely the cause of the low glass transparency. The silicide may furthermore act as nucleation sites for crystallization of glasses. TEM investigations on selected glasses showed homogeneous microstructures, with no evident substructural features, and selected area electron diffraction (SAED) patterns confirmed their amorphous nature. A high-resolution electron microscopy image of the Ca containing glass Ca-3 (cf. Table 1) is shown in Fig. 1. No evidence of metallic inclusions, phase separation, or other heterogeneities was found on examining several areas, and it was concluded that the glasses were microstructurally homogeneous.

It was found that the synthesis process involves dissociation of some of the components, resulting in deviation from the nominal compositions. The determined glass compositions are listed in Table 1 and nominal and determined AE (Mg, Ca, Sr, Ba) elements contents compared in Fig. 2. The elemental analyses shows that the prepared glasses had considerably lower contents of nitrogen and modifiers (loss of Si is less evident) than the starting mixtures, and that a loss of these elements thus had occurred at the comparatively high preparation temperatures used. The losses were found to increase for increasing temperature and, to a smaller extent, with increasing holding time. The losses may

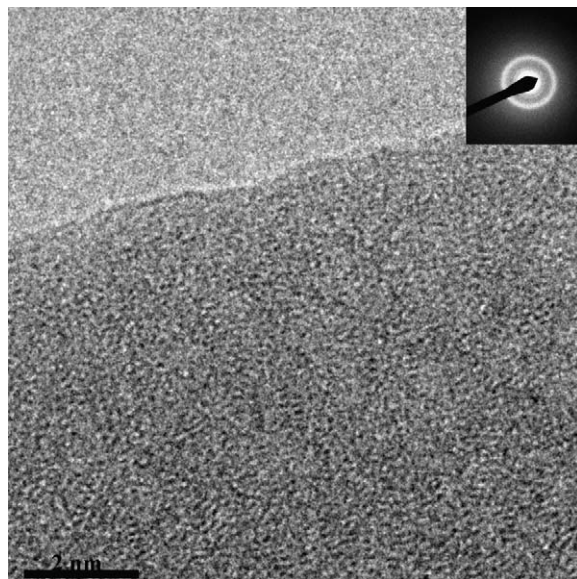


Fig. 1. A HRTEM image with corresponding electron-diffraction pattern (inset) of the Ca–Si–O–N glass Ca-3 (composition Ca_{8.03}Si₁₀O_{17.92}N_{6.65}).

partly be due to the decomposition reaction proposed by Messier and Deguire, whereby Si departs as gaseous SiO.³³ The reaction implies, however, the formation of elemental Si, whereas the glasses contain only minor amounts of elemental Si as evidenced by TEM investigations. The Mg losses were high, while losses of Ba were less evident. The smallest losses of nitrogen were observed for the Mg containing glasses and the largest ones for the Ba containing glasses. This indicates that the Mg has high reactivity toward the nitrogen. The cation compositions range from 13 to 37 e/o (9–24 at%) AE and the anion compositions from 14 to 42 e/o (6–19 at%) of N. The variation of AE content is accompanied with the variation of N content.

3.2. Density, molar volume and compactness

Measured densities and calculated molar volumes and compactness for the glasses are given in Table 2. The variation of the density as a function of AE contents is shown in Fig. 3. The

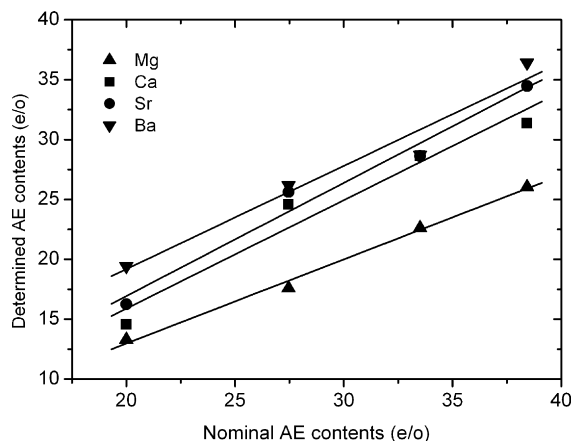


Fig. 2. Comparison of the nominal and determined AE (Mg, Ca, Sr, Ba) contents for AE–Si–O–N glasses.

Table 2

Physical properties of AE–Si–O–N glasses: glass designation, density (ρ), molar volume (MV), competence (C), cation field strength (CFS), glass transition temperature (T_g), crystallization temperature (T_c), hardness (H_v) and refractive index (n). Numbers in parenthesis are estimated standard deviations.

Glass ID	Density (g/cm ³)	MV (cm ³ mol ⁻¹)	C	CFS (Å ⁻²)	T_g (°C)	T_c (°C)	H_v (GPa)	n
Mg-1	2.78	7.23	0.56	3.858	910	1150	9.2 (4)	1.62
Mg-2	2.81	7.14	0.57	3.858	960	1195	10.5 (3)	1.65
Mg-3	2.83	7.12	0.57	3.858	995	1201	11.1 (1)	1.63
Mg-4	2.86	7.03	0.58	3.858	1020	1220	12.1 (6)	1.67
Ca-1	2.85	7.57	0.56	1.780	820	935	8.2 (2)	1.63
Ca-2	2.93	7.70	0.56	1.780	885	953	8.8 (8)	1.68
Ca-3	3.01	7.66	0.57	1.780	920	1048	9.3 (5)	1.72
Ca-4	3.03	7.70	0.57	1.780	955	1074	9.4 (8)	1.74
Sr-1	3.02	8.87	0.50	1.366	800	930	8.2 (29)	1.66
Sr-2	3.51	8.73	0.53	1.366	870	960	8.8 (8)	1.74
Sr-3	3.72	8.60	0.55	1.366	910	1060	9.3 (5)	1.77
Sr-4	3.96	8.67	0.55	1.366	940	1106	9.4 (8)	1.82
Ba-1	3.25	10.46	0.45	1.050	795	1010	8.1 (1)	1.71
Ba-2	3.77	10.39	0.48	1.050	848	1048	8.5 (2)	1.79
Ba-3	3.89	10.55	0.48	1.050	870	1086	9.1 (9)	1.84
Ba-4	4.16	11.22	0.47	1.050	890	1066	9.2 (7)	1.93

density of the Mg containing glasses shows the lowest values of while the density of Ba containing glasses shows the highest values. For Mg glasses the density values varies between 2.78 and 2.86, for Ca glasses between 2.85 and 3.03, for Sr glasses between 3.02 and 3.96 and for Ba glasses between 3.25 and 4.16 g/cm³. The regression analysis for Sr and Ba containing glasses yields $\rho = 2.28 (2) + 0.036 (5) \cdot [\text{Sr}] + 0.012 (7) \cdot [\text{N}]$, g/cm³, $R^2 = 0.98$ and $\rho = 2.52 (5) + 0.028 (8) \cdot [\text{Ba}] + 0.017 (6) \cdot [\text{N}]$, g/cm³, $R^2 = 0.96$, with Sr, Ba and N concentrations in e/o, demonstrating that the density variations depend primarily on the AE content. These results is in agreement with those found for RE element containing oxynitride glasses,^{10,34,35} for which the density increases with increasing atomic weight of the RE element. The increase in density with Sr and Ba content can be attributed to the large atomic weight of Sr and Ba, while smaller increases with N content may be due to a significant fraction of three-coordinated N in the glass. The molar volume (MV) values increase from Mg to Ba containing glasses. Ba glasses have the highest values of molar volume (e.g. 10.46–11.22 cm³/mol). It may also be added, that in our previous studies of Ca–Si–O–N²⁸ and Sr–Si–O–N²⁹ glasses, we found that increasing N con-

tent diminishes the MV and increasing modifier cation content increase it. Mg containing glasses shows high values of fraction compactness (e.g. 0.58) compared to the Ba containing glasses (e.g. 0.46).

3.3. Glass transition and crystallization temperatures

For silicate glasses, a high T_g is associated with a high strength of chemical bonding and a high polymerization degree of the network. Observed glass transition temperatures, T_g , and crystallization temperatures, T_c , for AE–Si–O–N glasses with different amounts of modifiers and N contents are listed in Table 2. A DTA recording for an Ca_{8.03}Si₁₀O_{17.92}N_{6.65} glass sample (Ca-3 in Table 2) is shown in Fig. 4. The T_g values varies between 795 and 1020 °C and shows clear trends, that T_g decreases in the series Mg, Ca, Sr, Ba, with Ba containing glasses having the lowest glass transition and crystallization temperatures. The average temperature difference between T_g and T_c is approximately 200 °C.

The comparatively low T_g values are similar to those determined by Videau et al.²² for M–Si–Al–O–N glasses with

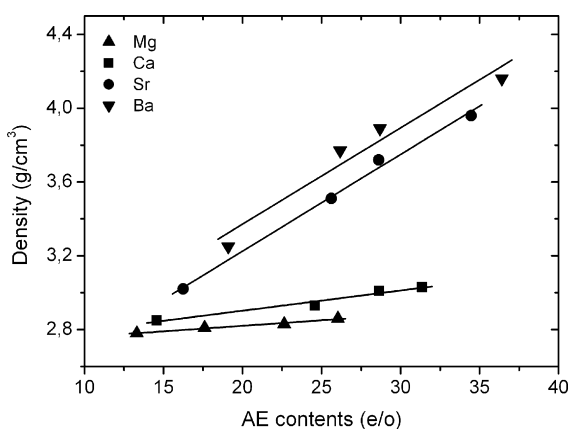


Fig. 3. Glass density as a function of amount of AE for AE–Si–O–N glasses.

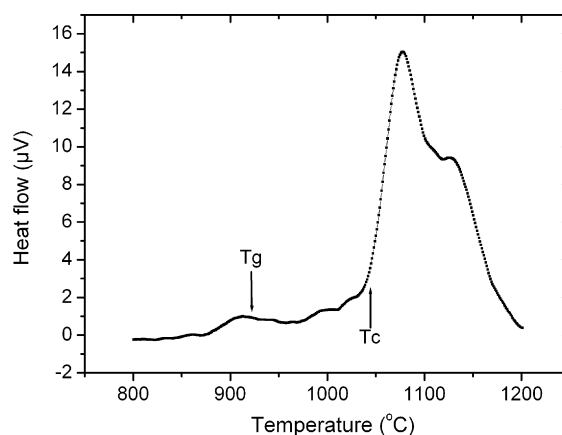


Fig. 4. DTA recording for Ca_{8.03}Si₁₀O_{17.92}N_{6.65} (sample no. Ca-3).

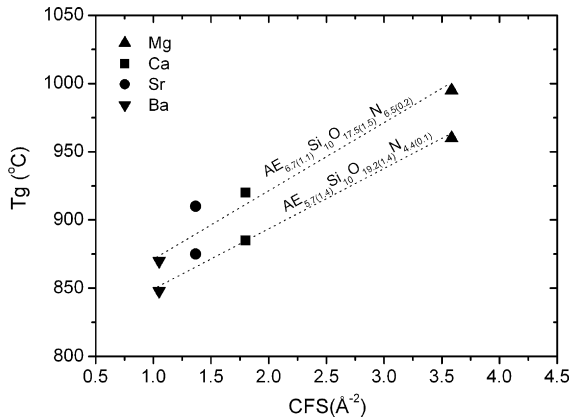


Fig. 5. Glass transition temperature as a function of CFS for AE-Si-O-N glasses.

$M = \text{Mg-Ca-Ba}$ or Li. Fig. 5 shows that the T_g increase with increasing CFS, similar phenomena was also observed for RE oxynitride glasses.^{10,17,18,36,37} Drew et al.,¹² however, found for $M\text{-Si-Al-O-N}$ glasses with $M = \text{Mg, Ca}$, slightly higher T_g values for the Ca glasses.

Fig. 6 shows that there is a significant increase in T_g and T_c with increasing nitrogen content. Since an increase in nitrogen content by all accounts increases the cross-linking of the glass network, the glass transition temperature is expected to increase as the nitrogen content of the glass increases. An increase in the glass transition temperature with increasing nitrogen content has also been found for other oxynitride glasses.^{17,22,38–41} A fit of the data to a linear dependence of T_g on both N and Ba contents yielded $T_g = 738(42) + 3(2) \cdot [\text{N}] + 1(4) \cdot [\text{Ba}]$, with $R^2 = 0.97$. The data thus indicate that the Ba content has far less effect on T_g than the N content. However, the separate effects of the modifier and N contents on physical properties are difficult to ascertain because of the strong correlation of the modifier and N contents.

3.4. Vickers hardness

The Vickers hardness data are given in Table 2 and plotted versus N content in Fig. 7 for Mg, Ca, Sr and Ba glasses. The

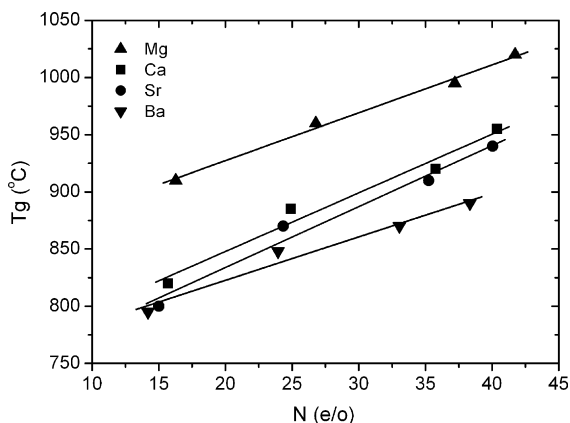


Fig. 6. Glass transition temperature as a function of N content for AE-Si-O-N glasses.

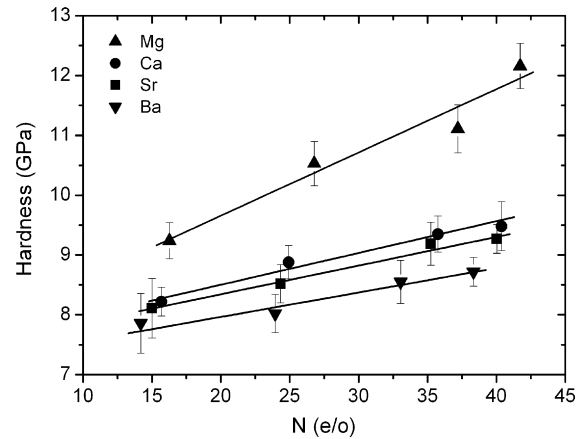


Fig. 7. Glass microhardness as a function of N content for AE-Si-O-N glasses.

Vickers hardness shows a variation between 8.1 and 12.2 GPa. A linear regression fit on both N and Ba content yielded $H_v = 7.42(5) + 0.048(2) \cdot [\text{N}] - 0.018(7) \cdot [\text{Ba}]$, with $R^2 = 0.95$. The data in AE systems indicate, however, that there is also a dependence on the modifier content. The increase in microhardness with increasing N content implies that the incorporation of nitrogen into the glass network strengthens the glass structure. This has been attributed to the presence of three-coordinated nitrogen.^{8,20,42–45} However, an increase in hardness with nitrogen content was observed also for high-nitrogen content La-Si-O-N²⁶ glasses with high X:Si [X = O, N] ratios, thus implying very fragmented networks, suggesting that there might be other causes for the observed increase in hardness. The replacing of one modifier for another in the AE-Si-O-N systems, evidently effect significant changes in hardness. Glasses in the Mg system shows the highest observed hardness being 12.2 GPa. The lower hardness values for the Ba substituted glasses agrees with the findings of Tredway and Risbud,²⁴ who reported hardness values for Ba-Si-Al-O-N glasses that are lower than by us reported values for Ca-Si-O-N and Sr-Si-O-N glasses. Hardness is often related to the CFS since it reflects the strength of the bonds in a material. For the present glasses, the hardness increases with increasing CFS of the AE element as shown in Fig. 8, corresponding to a strengthening of the glass by an

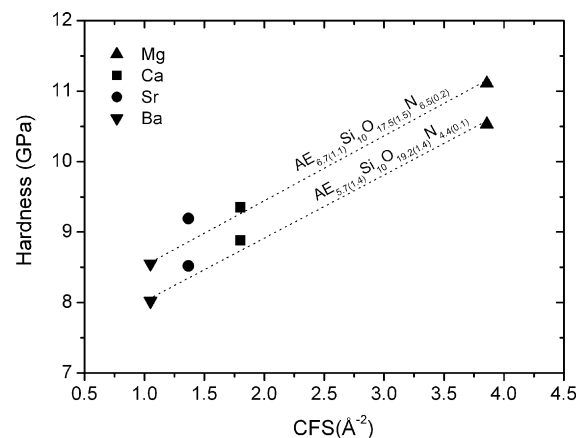


Fig. 8. Glass microhardness as a function of CFS for AE-Si-O-N glasses.

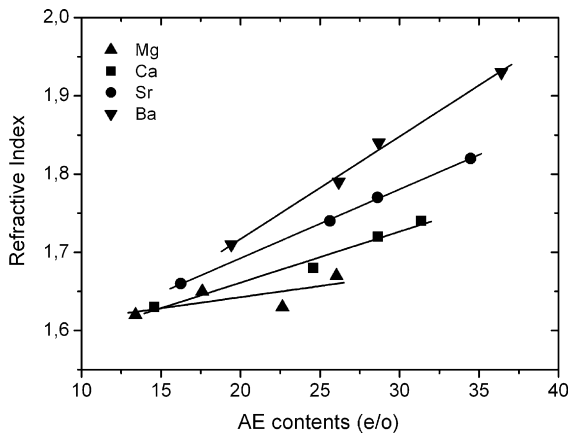


Fig. 9. Glass refractive index as a function of amount of AE for AE-Si-O-N glasses.

increasing strength of the AE-O bonds. The results imply that the AE element bonding contributes significantly to the strength of the glasses. A linear increase of microhardness with CFS agrees with findings for RE-Si-Al-O-N glasses.^{19–22} These results imply that the alkaline earths also contribute significantly to the glass network strength, in addition to the well known increase with increasing nitrogen content.

3.5. Refractive index

The results presented in Table 2 and Fig. 9 show that there are significant changes of the refractive index (n) upon substituting one AE element by another AE element. The refractive index at 640 nm varies from 1.62 for Mg containing glasses to 1.93 for Ba containing glasses. The refractive index increase with increasing content of AE elements except from Mg.

A linear regression fit yielded $n = 1.48 (2) + 0.002 (2) \cdot [N] + 0.009 (1) \cdot [Ba]$, with $R^2 = 0.99$. The refractive index is thus found to increase predominantly with the Ba content, but also with N content. A trend for n to increase with increasing amount of Sr was also observed for Sr-Si-O-N²⁹ glasses. Shelby⁴⁴ also found a trend toward increasing refractive index with increasing CaO content for calcium aluminosilicate oxide glasses. The Ba glasses exhibits higher values of refractive index than the Mg, Ca and Sr. The increase of refractive index can be attributed to increased polarizability of the modifier ions rather than significant changes in the glass structure.

4. Conclusions

Homogeneous glasses in AE-Si-O-N systems (AE = Mg, Ca, Sr or Ba) containing high amount of nitrogen (ca. 42 equiv.%) and alkaline-earth elements (ca. 37 equiv.%) have been prepared by heat-treating mixtures of AEH₂, SiO₂ and Si₃N₄ powders in nitrogen atmosphere. The colors of these glasses vary depending on the alkaline-earth elements used and their concentrations. The results show that the properties of AE-Si-O-N glasses, such as density, molar volume, glass transition and crystallization temperatures, hardness, and refractive index are affected by the

amount of nitrogen as well as by the modifiers. The density and molar volume increases substantially with an increase in the AE atomic mass. Ba containing glasses show high values of density and molar volume compare to Mg, Ca and Sr containing glasses.

Glass transition temperatures and hardness are found to be higher for Mg containing glasses, and that both T_g and Vickers hardness varies linearly with the cation field strength. These results accord with previous findings that have shown increasing values for these properties with increasing CFS of the modifier ions. In each case, the properties for a given composition correlate with the change in cationic field strength of the AE, consistent with a strengthening of the network by an increasing in the strength of AE-O bonds. These results imply that the alkaline earths also contribute significantly to the properties, in addition to the well known effect on properties with increasing nitrogen content. The Ba glasses exhibit higher values of refractive index than the Sr, Ca and Mg glasses.

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References

1. Jack KH, The role of additives in the densification of nitrogen ceramics. Final Tech. Rept., European research office, U.S. army, Grant No. DAERO-76-G-067; 1977.
2. Hampshire S. The role of additives in the pressureless sintering of nitrogen ceramics for engine applications. *Metals Forum* 1984;7(3):162–70.
3. Riley FL. Silicon nitride and related materials. *Journal of the American Chemical Society* 2000;83(2):245–65.
4. Loehman RE. Oxynitride glasses. *Journal of Non-Crystalline Solids* 1980;42(1–3):433–45.
5. Hampshire S, Drew RAL, Jack KH. Oxynitride glasses. *Physics and Chemistry of Glasses* 1985;26(5):182–6.
6. Hampshire S. Oxynitride glasses and their properties – an overview. *Key Engineering Materials* 2003;247:155–60.
7. Messier DR, Broz A. Microhardness and elastic-moduli of Si-Y-Al-O-N glasses. *Journal of the American Chemical Society* 1982;65(8):C123–123.
8. Coon DN, Rapp JG, Bradt RC, Pantano CG. Mechanical-properties of silicon-oxynitride glasses. *Journal of Non-Crystalline Solids* 1983;56(1–3):161–6.
9. Lemerrier H, Rouxel T, Fargeot D, Besson JL, Piriou B. Yttrium SiAlON glasses: structure and mechanical properties – elasticity and viscosity. *Journal of Non-Crystalline Solids* 1996;201(1–2):128–45.
10. Becher PF, Waters SB, Westmoreland CG, Riester L. Compositional effects on the properties of Si-Al-Re-based oxynitride glasses (RE = La, Nd, Gd, Y, or Lu). *Journal of the American Chemical Society* 2002;85(4):897–902.
11. Rouxel T, Dely N, Sangleboeuf JC, Deriano S, LeFloch M, Beuneu B, Hampshire S. Structure-property correlations in Y-Ca-Mg-sialon glasses: physical and mechanical properties. *Journal of the American Chemical Society* 2005;88(4):889–96.
12. Drew RAL, Hampshire S, Jack KH. Nitrogen glasses. *Proceedings of the British Ceramic Society* 1981;31:119–32.
13. Peterson IM, Tien TY. Thermal-expansion and glass-transition temperatures of Y-Mg-Si-Al-O-N glasses. *Journal of the American Chemical Society* 1995;78(7):1977–9.

14. Hakeem AS, Dauce R, Leonova E, Eden M, Shen ZJ, Grins J, Esmailzadeh S. Silicate glasses with unprecedented high nitrogen and electropositive metal contents obtained by using metals as precursors. *Advanced Materials* 2005;**17**(18):2214–6.
15. Pomeroy MJ, Nestor E, Ramesh R, Hampshire S. Properties and crystallization of rare-earth Si–Al–O–N glasses containing mixed trivalent modifiers. *Journal of the American Chemical Society* 2005;**88**(4):875–81.
16. Pomeroy MJ, Mulcahy C, Hampshire S. Independent effects of nitrogen substitution for oxygen and yttrium substitution for magnesium on the properties of Mg–Y–Si–Al–O–N glasses. *Journal of the American Chemical Society* 2003;**86**(3):458–64.
17. Ohashi M, Nakamura K, Hiraio K, Kanzaki S, Hampshire S. Formation and properties of Ln–Si–O–N glasses (Ln = lanthanides or Y) (vol. 78, p. 71, 1995). *Journal of the American Chemical Society* 1995;**78**(4):1136–136.
18. Murakami Y, Yamamoto H. Properties of oxynitride glasses in the Ln–Si–Al–O–N systems (Ln = rare-earth). *Nippon Seramikusu Kyokai Gakujutsu Ronbunshi-Journal of the Ceramic Society of Japan* 1994;**102**(3):231–6.
19. Pastuszak R, Verdier P. M–Si–Al–O–N glasses (M = Mg, Ca, Ba, Mn, Nd), existence range and comparative-study of some properties. *Journal of Non-Crystalline Solids* 1983;**56**(1–3):141–6.
20. Homeny J, McGarry DL. Preparation and mechanical-properties of Mg–Al–Si–O–N glasses. *Journal of the American Chemical Society* 1984;**67**(11):C225–7.
21. Sakka S, Kamiya K, Yoko T. Preparation and properties of Ca–Al–Si–O–N oxynitride glasses. *Journal of Non-Crystalline Solids* 1983;**56**(1–3):147–52.
22. Videau JJ, Etourneau J, Rocherulle J, Verdier P, Laurent Y. Structural approach of sialon glasses: M–Si–Al–O–N. *The Journal of Experimental Biology* 1997;**17**(15–16):1955–61.
23. Drew RAL, Hampshire S, Jack KH. The preparation and properties of oxynitride glasses. In: by FL, Riley, editors. *Progress in nitrogen ceramics*. The Hague: Martinus Nijhoff Publishers; 1983. p. 323–30.
24. Tredway WK, Risbud SH. Melt processing and properties of barium–sialon glasses. *Journal of the American Chemical Society* 1983;**66**(5):324–7.
25. Shaw TM, Thomas G, Loehman RE. Formation and microstructure of Mg–Si–O–N glasses. *Journal of the American Chemical Society* 1984;**67**(10):643–7.
26. Hakeem AS, Grins J, Esmailzadeh S. La–Si–O–N glasses – Part II: vickers hardness and refractive index. *The Journal of Experimental Biology* 2007;**27**(16):4783–7.
27. Hakeem AS, Grins J, Esmailzadeh S. La–Si–O–N glasses – Part I. Extension of the glass forming region. *The Journal of Experimental Biology* 2007;**27**(16):4773–81.
28. Sharafat A, Grins J, Esmailzadeh S. Glass-forming region in the Ca–Si–O–N system using CaH₂ as Ca source. *The Journal of Experimental Biology* 2008;**28**(14):2659–64.
29. Sharafat A, Forslund B, Grins J, Esmailzadeh S. Formation and properties of nitrogen rich strontium silicon oxynitride glasses. *Journal of Materials Science* 2009;**44**:664–70.
30. Shannon RD. Revised effective ionic-radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A* 1976;**32**(September (1)):751–67.
31. Anstis GR, Chantikul P, Lawn BR, Marshall DB. A critical-evaluation of indentation techniques for measuring fracture-toughness.1. Direct crack measurements. *Journal of the American Chemical Society* 1981;**64**(9):533–8.
32. Leonova E, Hakeem AS, Jansson K, Stevansson B, Shen Z, Grins J, Esmailzadeh S, Eden M. Nitrogen-rich La–Si–Al–O–N oxynitride glass structures probed by solid state NMR. *Journal of Non-Crystalline Solids* 2008;**354**(1):49–60.
33. Messier DR, Deguire EJ. Thermal-decomposition in the system Si–Y–Al–O–N. *Journal of the American Chemical Society* 1984;**67**(9):602–5.
34. Menke Y, Peltier-Baron V, Hampshire S. Effect of rare-earth cations on properties of sialon glasses. *Journal of Non-Crystalline Solids* 2000;**276**(1–3):145–50.
35. Lofaj F, Deriano S, LeFloch M, Rouxel T, Hoffmann MJ. Structure and rheological properties of the RE–Si–Mg–O–N (RE = Sc, Y, La, Nd, Sm, Gd, Yb and Lu) glasses. *Journal of Non-Crystalline Solids* 2004;**344**(1–2):8–16.
36. Lofaj F, Satet R, Hoffmann MJ, de Arellano Lopez AR. Thermal expansion and glass transition temperature of the rare-earth doped oxynitride glasses. *The Journal of Experimental Biology* 2004;**24**(12):3377–85.
37. Ramesh R, Nestor E, Pomeroy MJ, Hampshire S. Formation of Ln–Si–Al–O–N glasses and their properties. *The Journal of Experimental Biology* 1997;**17**(15–16):1933–9.
38. Sun EY, Becher PF, Hwang SL, Waters SB, Pharr GM, Tsui TY. Properties of silicon–aluminum–yttrium oxynitride glasses. *Journal of Non-Crystalline Solids* 1996;**208**(1–2):162–9.
39. Hampshire S, Nestor E, Flynn R, Besson JL, Rouxel T, Lemerrier H, Gour-sat P, Sebai M, Thompson DP, Liddell K. Yttrium oxynitride glasses – properties and potential for crystallization to glass-ceramics. *The Journal of Experimental Biology* 1994;**14**(3):261–73.
40. Loehman RE. Preparation and properties of yttrium–silicon–aluminum oxynitride glasses. *Journal of the American Chemical Society* 1979;**62**(9–10):491–4.
41. Hakeem AS. Novel route of oxynitride glass synthesis and characterization of glasses in the Ln–Si–O–N and Ln–Si–Al–O–N systems. Ph.D. thesis. Stockholm University; 2007.
42. Hampshire S, Pomeroy MJ. Oxynitride glasses. *International Journal of Applied Ceramic Technology* 2008;**5**(2):155–63.
43. Lofaj F, Hvizdos P, Dorcakova F, Satet R, Hoffmann MJ, de Arellano-Lopez AR. Indentation moduli and microhardness of RE–Si–Mg–O–N glasses (RE = Sc, Y, La, Sm Yb and Lu) with different nitrogen content. *Materials Science and Engineering A: Structural Materials Properties Microstructure and Processing* 2003;**357**(1–2):181–7.
44. Shelby JE. Formation and properties of calcium aluminosilicate glasses. *Journal of the American Chemical Society* 1985;**68**(3):155–8.
45. Brow RK, Pantano CG. Nitrogen coordination in oxynitride glasses. *Journal of the American Chemical Society* 1984;**67**(4):C72–4.