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La–Si–O–N glasses
Part I. Extension of the glass forming region

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Abstract

The nitrogen-rich part of the glass forming region in the La–Si–O–N system has been the subject of a comprehensive study. Glasses were prepared by heating powder mixtures of La metal, Si_3N_4 and SiO_2 in a nitrogen atmosphere at 1650–1800 °C. By this new synthesis route, glasses containing up to 68 e/o of N and 62 e/o of La were prepared, showing that the glass forming region is significantly larger than previously reported. The glasses were characterized by elemental analysis, differential thermal analysis, X-ray powder diffraction, and scanning electron microscopy. They were found to be X-ray amorphous and homogenous, with the majority of them containing small amounts of crystalline La silicides and elemental Si. Glass transition temperatures (T_g) were found to vary between 900 and 1100 °C and crystallization to occur typically 120 °C above T_g. The forming of the glasses was investigated by characterizing samples taken out at various steps of the heating cycle. The results indicate that the glass formation is strongly dependent on reaction kinetics. A strong exothermal reaction occurs at temperatures 900–1100 °C, leading to the formation of assemblies of amorphous and crystalline (oxy)nitride phases that melt upon further heating at 1650–1800 °C.

Keywords: Oxynitride; Nitride; Glass; Silicate; Lanthanum

1. Introduction

Silicon based oxynitride glasses can be regarded as derived from corresponding oxide glasses by partial replacement of oxygen by nitrogen. Nitrogen is in general thought of as having a similar structural role as oxygen, except that part of it may link three silicon tetrahedra. The importance of an oxynitride liquid phase during sintering and densification of Si_3N_4 based ceramics is well known. This has led to studies on the preparation and property characterization of bulk oxynitride glasses in the systems M–Si–(Al)–O–N (M = Na,[1–5] Li,[3,6,14] Sc,[7,15] Ba,[3,8] Mn,[3,9,10] Y,[11,16,17,18] La,[12,17,18] Mg,[8,13–16] Ca,[5,9,10,14] Nd,[9,17,18,20,22] Ce,[18,20,21] Sm,[17,20,22] Gd,[17,19,22] Eu,[20] Dy,[17,18,20,22] Ho,[20] and Er[17,18,20,22] Yb,[17,22]). The studies have shown that the oxynitride glasses, in comparison with related oxide glasses, generally have higher elastic modulus and hardness values.[20,23–26] It has also been proposed that lanthanide Si–O–N glasses may exhibit higher refractoriness than similar glasses also containing Al.[18] Other studies show oxynitride glasses to have a high chemical resistance, making them potential candidates for nuclear waste disposal.[27] More recently, they have also been considered as host materials for luminescent ions in pigments or light emitting diodes,[28] and as reinforcement in composites for optical applications.[29]

For oxynitride glasses that do not contain aluminium, *i.e.* M–Si–O–N systems, most of the early work concerned glasses with M = Mg, Ca, Y and Ce.[13,21,30] It was found that addition of nitrogen in the form of Si_3N_4 promotes glass formation and that the glass forming regions are relatively small.[30] In the case of Mg, glasses were obtained with 15–28 e/o of Mg and 10–12 e/o of N.[13] For lanthanide M, reported data are restricted to M = Ce and La. In the Ce–Si–O–N system, formation of clear glasses was observed for nitrogen contents less than 20 e/o and with ca. 40 e/o of Ce.[21] For higher nitrogen contents, the glasses became opaque, and phase separation was observed above 30 e/o of N. It was later proposed that similar glass forming regions are probably valid for the lanthanides La, Nd, Dy, and Er.[18] For La, the maximum incorporable amount of N by traditional synthesis methods is ∼18 e/o.[18] Nitrogen contents reaching up to 18 at.% (38 e/o) have, however, been achieved by synthesis

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under a nitrogen gas pressure of 3 MPa.[31] The glass forming regions, and nitrogen contents, of oxynitride glasses are significantly increased upon adding Al as a component in the systems, *e.g.* up to ∼30 e/o of N can be incorporated in the La–Si–Al–O–N system.[32]

Oxynitride glasses are frequently grey or greyish-brown in colour,[33] with the colouration depending on the network modifier and concentration of nitrogen. The intensity of the colour is not always higher for a high nitrogen content glass,[24] and Makishima et al.[12] succeeded in preparing a clear glass containing a large amount of N (18 at.%, or 38 e/o) in the La–Si–O–N system. Shaw et al.[13] found that the stability of Mg–Si–O–N melts was strongly dependent on their compositions, with frothing or bubbling taking place for high contents of SiO_2 and Si_3N_4. They observed Si particles with diameters of about 0.5 μm in their glasses and found these to be a probable cause for the colour. Messier and Deguire[34] likewise concluded that Si particles are responsible for the grey colour of Si–Y–A1–O–N glasses. They proposed that the formation of the elemental Si particles does not arise from a direct dissociation of Si_3N_4 into $Si_{(l)}$ and $N_{(g)}$, but from a decomposition reaction, at temperatures above ca. 1650 °C, of the form:

$$Si_3N_{4(s)} + SiO_{2(s)} \Rightarrow 2SiO_{(g)} + 2Si_{(l)} + 2N_{2(g)}$$

Thermodynamic considerations[34,35] show that this reaction cannot be suppressed much by increasing the nitrogen gas pressure, in agreement with their observations that the elemental silicon content in the glasses was not significantly reduced by applying high nitrogen gas pressures. Higher transparencies were furthermore observed for compositions that could be melted at a lower temperature, 1450 °C, at which the decomposition of Si_3N_4 is expected to be significantly smaller. However, in apparent contradiction to these interpretations, the presence of any crystalline phase was ruled out in another study of Y–Si–Al–O–N glasses,[36] on the basis of the absence of observable electron diffraction patterns from such a phase.

Silicon oxynitride and sialon glasses have traditionally been synthesized by melting mixtures containing Si_3N_4, SiO_2 and additional metal oxides. The nitrogen content achievable is typically then ca. 20 e/o. We have recently developed an alternative synthesis route, in which the electropositive elements are used in the form of metals that convert to nitrides by reaction with the nitrogen gas atmosphere. By this route, we have prepared a range of new oxynitride glasses that contain significantly higher contents of both nitrogen and additives.[37]

2. Experimental

The oxynitride glasses were prepared from powder mixtures of La metal (ChemPure, 99.9%), Si_3N_4 (UBE, SNE10), and SiO_2 (Aerosil 50). Batches of 10 g were mixed and ground inside a glove box under argon atmosphere. The syntheses were made in niobium metal crucibles in N_2 gas atmosphere, serving as the nitridation source for the La metal.[37] The mixtures were melted at 1650–1800 °C, depending on the composition, using a radio frequency furnace. The samples were heated up to 1400 °C in 10 min, held there for 1 h, and then heated up to the final temperature and held there for 1–4 h, depending on the composition. They were cooled so as to avoid build-up of internal stresses in the glasses as much as possible: down to 900 °C in 2 min, then from 900 to 500 °C in 30 min, and then further down to room temperature in 1 h maximum. Lanthanum metal was found to be highly reactive towards the nitrogen gas, as well as to the SiO_2 and Si_3N_4 powders, and a strong exothermal reaction was always observed around 900–1100 °C, the strength of the reaction increasing with the amount of La metal used.

Cation compositions were determined by energy-dispersive X-ray (EDX) point analyses on polished and graphite coated surfaces, using a JEOL 820 scanning electron microscope (SEM) equipped with a LINK AN10000 EDX system. Fifteen point analyses, on the average, were made for each glass. Anion contents were determined by combustion analysis (LECO equipment). X-ray powder diffraction (XRPD) patterns were recorded using a Guinier-Hägg camera and Cu Kα1 radiation. Densities were measured using the Archimedes method in water. Crushed pieces of glasses were used for differential thermal analysis (DTA) with a SETARAM TG-DTA 1600 for determination of glass transition (T_g) and crystallization (T_c) temperatures. The measurements were made up to 1400 °C in flowing argon atmosphere, using Pt cups and a heating rate of 25°/min. The onset point of an endothermic shift in the DTA curve was taken as representing T_g, and the onset of an exothermal peak as corresponding to T_c.

3. Results

3.1. The glass forming region

A total number of 120 different compositions were synthesized in order to determine the glass forming region in the La–Si–O–N system. The initial compositions are shown in the phase diagram given in Fig. 1(a), with circles representing compositions that resulted in glasses and crosses compositions that were found to be partially crystalline. 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 phase diagram, *i.e.* the SiO_2–LaN join, did not form glass if only SiO_2 and La metal were used (*e.g.*, samples 12 and 18 in Table 1). Such glasses were, however, comparatively easily obtained upon adding a small amount of La_2O_3, together with a compensating amount of Si_3N_4. Glass formation at the oxygen rich side of the diagram could not be investigated properly by the present method, due to oxidation of the Nb crucibles by La_2O_3 and SiO_2. We believe 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. This work is, however, focused on determining the glass forming region for La and N rich compositions.

Elemental analysis of the prepared glasses showed that they contained considerably lower contents of nitrogen and silicon than the starting mixtures, and thus that losses of

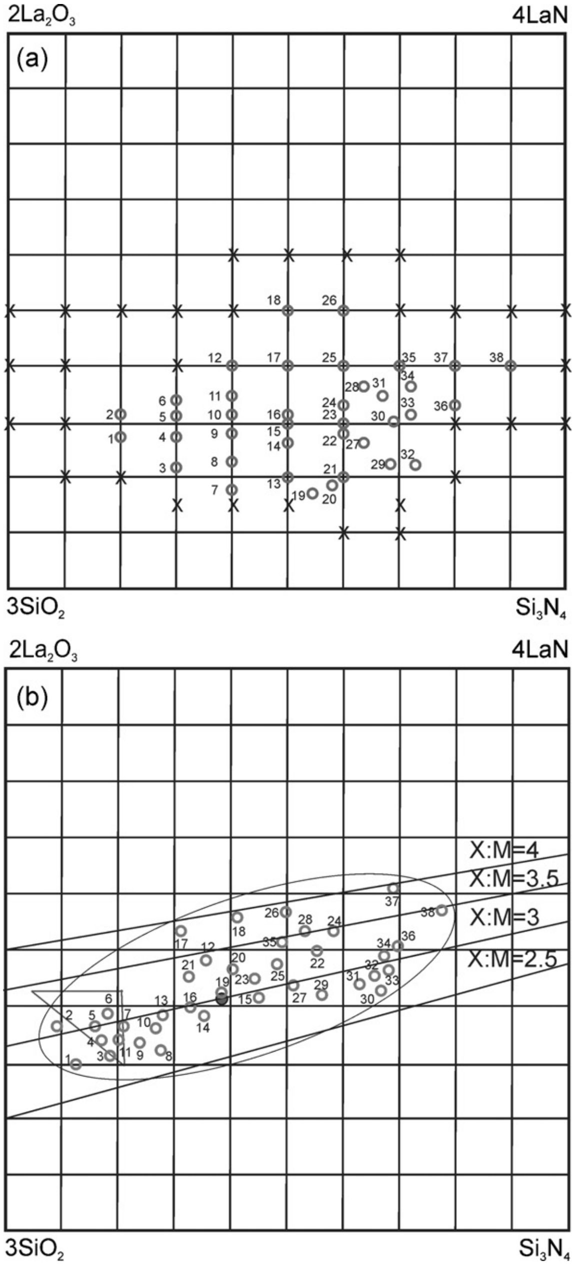

Fig. 1. (a) Starting mixtures for glasses prepared in the La_2O_3–SiO_2–LaN–Si_3N_4 system. Open circles represent formed glasses and crosses represent partially crystalline samples. (b) Glasses obtained in the La_2O_3–SiO_2–LaN–Si_3N_4 system. The triangle envelops previously prepared Ce–Si–O–N glasses,[21] and the filled circle shows one previously prepared La–Si–O–N glass.[12] The slanting lines show selected constant values for the ratio X:M = [O,N]/[Si].

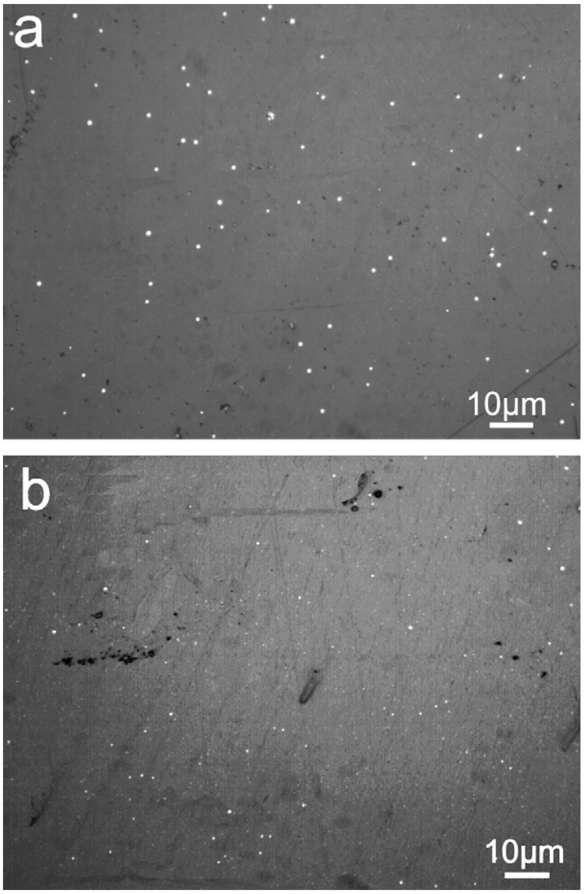

Fig. 2. Light micrographs showing the presence of La silicides in a glass (no. 35 in Table 1) held at 1800 °C for (a) 2 h and (b) 4 h.

these elements occur at the comparatively high preparation temperatures (1650–1800 °C) used. The determined glass compositions are tabulated in Table 1. The observed glass forming region is shown in Fig. 1(b), together with previously reported glass compositions in the systems M–Si–O–N with M = La and Ce.

In Fig. 1(b), lines have been included that show constant values of the ratio X:M = [O,N]/[Si]. Most of the obtained glasses have X:M ratios between 2.5 and 3.5, but some of them show values approaching 4. It is quite remarkable for silicon-based glasses to have such high values, since it apparently implies a very low connectivity of the tetrahedral frameworks. The high values suggest that the structures of the glasses differ in some fundamental way from those of previously investigated glasses with lower N contents. This issue is further addressed in the discussion section. The densities of the glasses were found to range from 4.2 to 5.4 g/cm^3, the density being strongly correlated with the La content.

All obtained glasses were opaque and generally had a deep brown colour. Approximately, half of them were found, by optical microscopy and SEM, to contain small amounts of spherical La silicide particles. The size of the particles ranged from, in rare cases, 5 μm down to a typical size of 1 μm and less. The amount of them was estimated as typically less than 1 vol.%, but was for some samples as high as 2–4 vol.%. The amounts showed no clear variation with glass composition or preparation temperature, but were found to decrease with increasing holding time. In Fig. 2, optical micrographs are shown for a sample (no. 23 in Table 1) prepared at 1800 °C for 2 and 4 h. Elemental silicon was not observed by SEM. Preliminary investigations by TEM showed that the glasses do contain very small amounts of small Si particles, but that the amounts are far less than those of the silicides.

Table 1
Data for prepared La–Si–O–N glasses; compositions of starting mixtures, determined glass compositions, La cation content in e/o, N content in e/o, the ratio X:M = [O,N]/[Si], glass transition temperatures (T_g), glass crystallization temperatures (T_c), density (ρ)

ID no.	Starting composition	Glass composition	La (e/o)	N (e/o)	X:M	T_g (°C)	T_c (°C)	ρ (g/cm^3)
1	$La_5Si_{10}O_{22}N_{3.67}$	$La_{5.81}Si_{10}O_{24.22}N_{2.99}$	30.3(5)	13.9(4)	2.72	954	1087	4.24
2	$La_6Si_{10}O_{23.2}N_{3.867}$	$La_{8.14}Si_{10}O_{29.164}N_{2.03}$	37.8(6)	9.2(3)	3.12	943	1042	4.48
4	$La_5Si_{10}O_{19.25}N_{5.5}$	$La_{7.62}Si_{10}O_{25.57}N_{3.90}$	36.3(4)	17.6(2)	2.95	979	1112	4.70
5	$La_6Si_{10}O_{20.3}N_{5.8}$	$La_{7.90}Si_{10}O_{26.56}N_{3.53}$	37.2(5)	15.6(7)	3.01	965	1094	4.44
6	$La_7Si_{10}O_{21.35}N_{6.1}$	$La_{8.15}Si_{10}O_{25.93}N_{4.19}$	37.9(8)	18.2(3)	3.01	981	1121	4.55
7	$La_3Si_{10}O_{14.7}N_{6.53}$	$La_{7.84}Si_{10}O_{26.17}N_{3.73}$	37.1(3)	17.3(6)	2.99	968	1086	4.69
8	$La_4Si_{10}O_{15.6}N_{6.933}$	$La_{7.06}Si_{10}O_{22.27}N_{5.55}$	34.6(6)	24.9(4)	2.78	987	1157	4.44
9	$La_5Si_{10}O_{16.5}N_{7.33}$	$La_{7.45}Si_{10}O_{23.59}N_{5.05}$	35.8(6)	21.9(3)	2.86	974	1130	4.56
10	$La_6Si_{10}O_{17.4}N_{7.73}$	$La_{7.59}Si_{10}O_{22.95}N_{5.62}$	36.27(3)	24.4(6)	2.86	980	1154	4.66
12	$La_{8.89}Si_{10}O_{20}N_{8.89}$	$La_{12.22}Si_{10}O_{24.01}N_{9.55}$	47.8(5)	35.3(3)	3.36	1053	1175	5.15
13	$La_{3.33}Si_{10}O_{12.5}N_{8.33}$	$La_{8.52}Si_{10}O_{23.25}N_{6.36}$	38.9(6)	27.1(7)	2.96	1030	1118	4.72
14	$La_5Si_{10}O_{13.75}N_{9.167}$	$La_{8.25}Si_{10}O_{20.28}N_{8.06}$	38.2(5)	34.1(3)	2.83	1075	1160	4.68
16	$La_6Si_{10}O_{14.5}N_{9.67}$	$La_{8.82}Si_{10}O_{20.89}N_{8.22}$	39.8(3)	33.4(4)	2.91	1063	1145	4.77
17	$La_{8.89}Si_{10}O_{16.67}N_{11.11}$	$La_{16.1}Si_{10}O_{29.68}N_{9.62}$	54.6(7)	31.3(5)	3.93	1008	1105	5.46
18	$La_{13.3}Si_{10}O_{20}N_{13.3}$	$La_{16.45}Si_{10}O_{26.24}N_{12.28}$	55.2(5)	40.1(4)	3.85	1010	1113	5.42
21	$La_{3.33}Si_{10}O_{10}N_{10}$	$La_{11.62}Si_{10}O_{23.89}N_{9.03}$	46.5(8)	34.1(3)	3.29	1030	1140	5.14
22	$La_5Si_{10}O_{11}N_{11}$	$La_{13.4}Si_{10}O_{16.78}N_{15.54}$	50.1(8)	56.9(3)	3.23	1067	1176	–
23	$La_{5.714}Si_{10}O_{11.4}N_{11.4}$	$La_{11.03}Si_{10}O_{20.42}N_{10.75}$	45.2(4)	43.3(8)	3.12	1086	1157	4.91
24	$La_{6.67}Si_{10}O_{12}N_{12}$	$La_{14.62}Si_{10}O_{18.4}N_{15.67}$	52.2(3)	58.3(6)	3.41	–	–	5.27
25	$La_{8.89}Si_{10}O_{13.3}N_{13.3}$	$La_{12.04}Si_{10}O_{19.7}N_{12.24}$	47.4(4)	45.8(7)	3.19	1090	1178	5.28
26	$La_{13.33}Si_{10}O_{16}N_{16}$	$La_{18.15}Si_{10}O_{23.02}N_{16.13}$	57.6(5)	49.1(3)	3.92	1057	1161	5.51
30	$La_8Si_{10}O_8N_{16}$	$La_{11.7}Si_{10}O_{11.53}N_{17.34}$	46.7(3)	65.7(4)	2.89	1061	1210	–
31	$La_{7.33}Si_{10}O_{10}N_{14}$	$La_{10.64}Si_{10}O_{12.92}N_{15.36}$	44.3(4)	62.6(5)	2.83	–	–	–
33	$La_6Si_{10}O_8N_{12}$	$La_{12.33}Si_{10}O_{9.42}N_{19.38}$	48.1(4)	67.9(5)	2.88	–	–	–
34	$La_{7.67}Si_{10}O_9N_{15}$	$La_{13.1}Si_{10}O_{12.57}N_{18.23}$	49.4(6)	66.8(3)	3.05	1072	1235	4.99
35	$La_{8.89}Si_{10}O_{10}N_{15.56}$	$La_{14.04}Si_{10}O_{19.39}N_{14.5}$	51.3(3)	48.9(6)	3.39	1062	1166	5.36
37	$La_{8.89}Si_{10}O_{6.67}N_{17.78}$	$La_{21.72}Si_{10}O_{10.11}N_{28.32}$	61.9(5)	67.3(3)	3.84	968	1103	5.51
38	$La_{8.89}Si_{10}O_{3.33}N_{20}$	$La_{18.08}Si_{10}O_{6.59}N_{27.03}$	57.5(6)	76.4(3)	3.36	1042	1265	5.45

Numbers in parenthesis are estimated standard deviations.

3.2. The synthesis route and reaction mechanisms

In order to shed light on the formation of the glasses and intermediate reactions, powder mixtures with compositions corresponding to $La_{5.71}Si_{10}O_{11.43}N_{11.43}$ (no. 23 in Table 1) were heat treated in a manner similar to preparing the glass, the heat treatments were interrupted at various stages, and the samples thus obtained, handled in inert atmosphere in order to minimise reaction with air, were characterized by XRPD and SEM. The heat treatment consisted of a slow first heating to ca. 900 °C, whereupon a strong exothermal reaction took place and the sample briefly attained a temperature, estimated by pyrometer, of ca. 1600–1800 °C. The samples were then consecutively slowly heated to 1200, 1400, and 1600 °C and held at each temperature for 1 h. Samples for characterization were acquired by interrupting the heating cycle at each of these temperatures after 10 min and 1 h. Because, it is not possible to reproduce the glass forming reaction in all its details by this procedure, due to additional necessary heating and cooling times, a more detailed study would require in-situ experiments, *e.g.* by real-time XRD or spectroscopic methods.

By XRPD, three predominant crystalline phases were clearly identified: pseudo-hexagonal $LaSiO_2N$[38] (ICSD no. 9752, PDF no. 33-0722), with a α-$CaSiO_3$ pseudo-wollastonite structure, apatite type $La_{10}Si_6O_{24}N_2$ (ICSD no. 91850, PDF no. 36-0571) and α-Si_3N_4 (PDF no. 41-0360). In addition, samples were found to contain smaller amounts of $La_4Si_2O_7N_2$ (ICSD no. 97631, PDF no. 36-0573) and $LaSi_2$ (ICSD no. 26663, PDF no. 06-0471). Representative XRPD patterns of samples containing these phases are shown in Fig. 3. In addition, some samples yielded weak reflections that could be assigned to La_3Si_2 (ICSD no. 44696, PDF no. 19-0660), La_2SiO_5 (PDF no. 40-0234), and, possibly, high-temperature cristobalite, SiO_2 (PDF no. 04-0359).

In summary, the samples were found to contain comparatively large amounts of oxygen-rich La oxynitride phases, unreacted Si_3N_4, and smaller amounts of La silicides. The relative amount of the dominant phase $LaSiO_2N$ increased with heating temperature, and it was the only identified crystalline phase in the sample heated to 1600 °C. The other two La oxy-nitride phases, $La_{10}Si_6O_{24}N_2$ and $La_4Si_2O_7N_2$, were observed in samples heated to 1200–1400 °C. The silicide $LaSi_2$ was found in all samples except the one heated to 1600 °C, whereas, La_3Si_2 was only found, in minute quantity, in the sample heated to 900 °C. Un-reacted Si_3N_4 was found in roughly equal amounts in samples heated to 900–1400 °C, whereas, the amount was significantly less in the samples heated to 1600 °C.

SEM images of polished surfaces showed that samples heated to comparatively low temperatures, 900–1200 °C, were quite porous, containing up to 100 μm large voids. The porosity clearly decreased with heating temperature, and samples heated to 1400–1600° exhibited nearly full density. Back-scattered

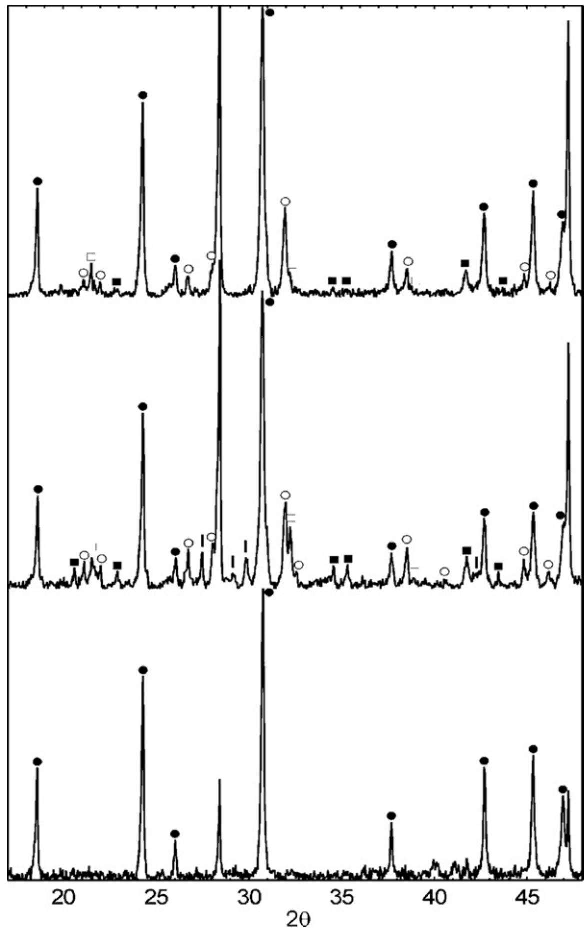

Fig. 3. XRPD patterns for samples heated to, from top to bottom, 900 °C/10 min, 1200 °C/1 h and 1600 °C/1 h. The marked phases are $LaSiO_2N$ (●), $La_{10}Si_6O_{24}N_2$ (○), α-Si_3N_4 (■), $LaSi_2$ (□) and $La_4Si_2O_7N_2$ (❙). The two unmarked strong reflections are from the internal Si standard used.

electron (BSE) images for samples heated to different temperatures are shown in Fig. 4. The two main phases observed for all samples were a glass phase and crystalline $LaSiO_2N$. The observed contrast from these phases is most easily seen in images of samples heated to comparatively high temperatures, *e.g.* Fig. 4(c). Energy-dispersive X-ray (EDX) analysis showed that the glass phase had a cation composition of 53.7(8)% La and 46.3(8)% Si. The composition did not to vary significantly with either heating temperature or spatial region. For samples heated to 1400–1600 °C, the microstructures that contain $LaSiO_2N$ crystallites, see Fig. 4(c, e and f), indicate that $LaSiO_2N$ is formed rapidly during cooling, and larger regions containing $LaSiO_2N$ and glass were often observed to alternate with regions containing only glass. This implies first that the real amounts, if indeed any, of $LaSiO_2N$ in the samples at temperatures 1400–1600 °C are not known. A crystallization of $LaSiO_2N$ upon cooling might be assisted by large-scale compositional fluctuations in the glass and/or the presence of undissolved particles, acting as primary nucleation sites. Secondly, for samples heated to lower temperatures, 900–1200 °C, the present glass and $LaSiO_2N$ have most probably formed during the rapid temperature increase and subsequent fast cooling that occur upon heating at ca. 900 °C. During this heat surge the samples briefly attained temperatures of ca. 1600–1800 °C.

The silicides $LaSi_2$ and La_3Si_2 were typically present as rounded crystallites. For lower heating temperatures these were often quite large, see Fig. 4(a and d), and surrounded by a layer containing a more La rich glass and Si_3N_4. For higher heating temperatures the spherical particles were typically smaller, ranging in size from 10 μm down, and homogeneously distributed through the samples, see Fig. 4(e and f). The results show that the La silicides gradually dissolve into the glass with increasing temperature and time. According to Bulaqnova et al.,[39] $LaSi_2$, a solid solution phase with compositions ranging from $LaSi_2$ to $LaSi_{1.65}$, melts congruently at 1730 °C, and La_3Si_2 melts peritectically at 1470 °C. The oxygen-rich oxynitride phases $La_{10}Si_6O_{24}N_2$ and $La_4Si_2O_7N_2$ could not be reliably differentiated by EDX analysis, due to their similar cation compositions. Larger, ca. 10 μm big, particles with corresponding compositions were observed for samples heated to 1200–1400 °C. Unreacted Si_3N_4 was found in two kinds of microstructures, see Fig. 4(d): as up to ca. 5 μm big crystals within the main glass matrix and in spherical 10–50 μm diameter regions containing a mixture of a La-richer glass and Si_3N_4. Because, the grain size of the initial Si_3N_4 powder was below 0.1 μm, this implies that a grain growth takes place for Si_3N_4. It can furthermore not be ruled out that part of the Si_3N_4 is also dispersed throughout the samples in the form of very small isolated grains.

The results show that a La-rich oxy-nitride glass forms during the heat surge that occurs upon heating at ca. 900 °C. When increasing the temperature from 900 to 1600 °C, the crystalline silicides and oxygen-rich oxy-nitride phases are progressively dissolved into the glass, and the materials consolidate. The large-scale inhomogeneities that remain in the samples after the heat surge are, however, expected to be difficult to dissolve without applying comparatively high temperatures.

3.3. Glass transition and crystallization temperatures

Observed glass transition temperatures, T_g, and crystallization temperatures, T_c are tabulated in Table 1 for 23 La–Si–O–N glasses. DTA recordings for two glasses are shown in Fig. 5. The glass transition temperatures range from 950 to 1100 °C, and crystallization temperatures from 1050 to 1250 °C. The average temperature difference between T_g and T_c is ca. 120 °C.

Although there is a general trend in the data that glasses with high N or high La contents tend to have high T_g values, the correlation for such dependence is not strong if one includes all glass compositions. However, by grouping the glasses according to their X:M values, dependencies on the N content can be seen for each of the different classes. Eleven out of the 23 glasses investigated have X:M values between 2.5 and 3, eight have X:M values between 3 and 3.5, while only four have X:M values between 3.5 and 4. The dependencies of T_g and T_c on nitrogen content for these classes are shown in Fig. 6. The T_g values remain comparatively constant for glasses with X:M between 2.5 and 3 up to ca. 25 e/o of N, but then appear to increase at higher N contents. For glasses with X:M between 3 and 3.5, T_g increases with increasing N content for 10 to ca. 50 e/o of N

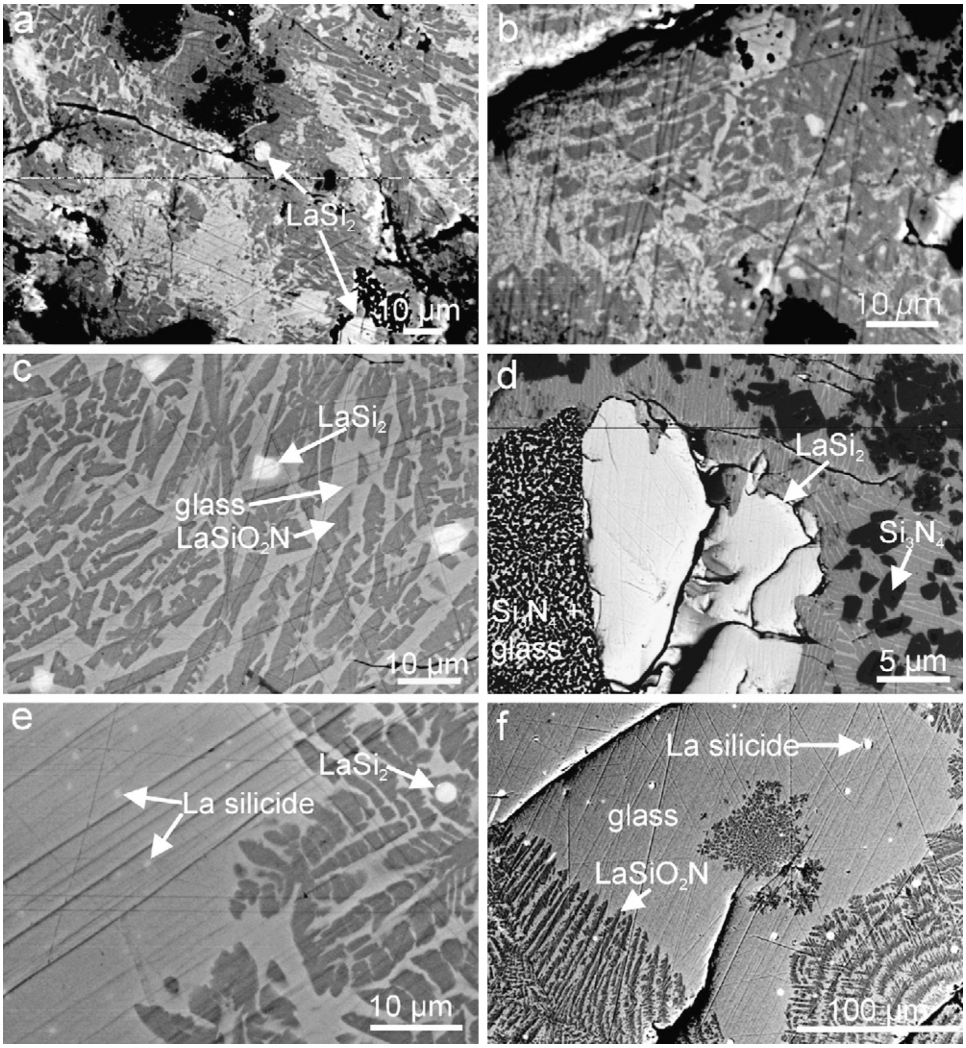

Fig. 4. SEM BSE images of samples heated to (a) 1200 °C/10 min, (b) 1400 °C/10 min, (c and d) 1400 °C/1 h, (e) 1600 °C/10 min and (f) 1600 °C/1 h.

and then decreases for higher N contents. For X:M ratios 3.5–4, the small number of observations indicate that T_g remains fairly constant for N contents between 30 and 70 e/o.

4 Discussion

The results show that the glass forming region in the La–Si–O–N system extends further into the nitrogen rich part than previous reports have indicated, and that X-ray amorphous glasses containing up to 68 e/o of N and 62 e/o of La can be prepared. Preliminary studies show that other lanthanide metals (Ce, Pr, Nd, Sm, Gd and Dy) form glasses in a similar manner. The formation of the glasses is clearly dependent on the precursors used and their reaction kinetics. The use of La metal instead of La oxide as "additive" has several advantages: (a) it provides for the preparation of nitrogen-rich compositions, since it effectively functions as a nitrogen source by reacting with the nitrogen atmosphere; (b) it is highly reactive towards Si_3N_4 and SiO_2, as evidenced by the formation of large amounts of various oxynitride phases at the beginning of the heat treatments; (c) intimate mixtures of intermediate phases are formed upon the exothermal reaction at 900–1100 °C, providing for improved reaction kinetics at further heating. The La metal used in the present study was furthermore in the form of a comparatively coarse powder, with grain sizes up to hundreds of microns. The large-scale inhomogeneities observed by SEM in partly reacted samples suggest that glasses could possibly be obtained at lower temperatures and/or in shorter times by using finer grained La metal, or alternatively LaH_3. Disadvantages of using La metal as precursor include a high cost and the need to work in an oxygen-and moisture-free atmosphere.

We hold it quite likely that the silicide particles cause the colourings of the glasses. The partially reacted samples contained smaller amounts of La silicides, implying that a part of the initial Si_3N_4 or SiO_2 is reduced at an early stage. The reaction mechanism for this reduction is not known, but it possibly involves a direct reaction between La metal and Si_3N_4 to produce $La_xSi_y + N_2$ or LaN + Si, with a subsequent reaction of La and Si. The former reaction implies a loss of nitrogen gas, and it could thus in part account for the observed differences between starting and final compositions. The silicides in these samples were present both in the form of larger grains and as smaller spherical

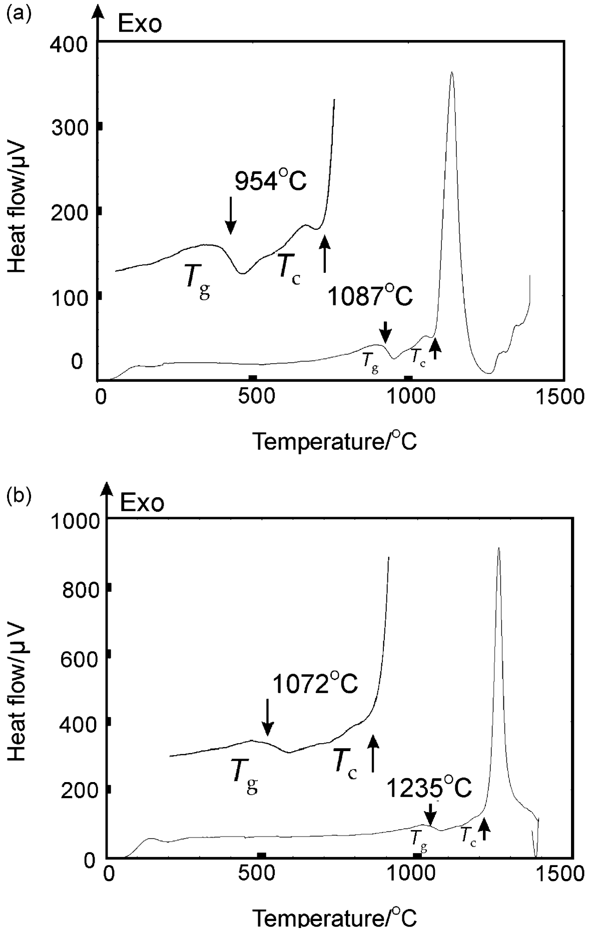

Fig. 5. DTA recordings for samples (a) $La_{5.81}Si_{10}O_{24.22}N_{2.99}$ (no. 1) and (b) $La_{13.1}Si_{10}O_{12.57}N_{18.23}$ (no. 34).

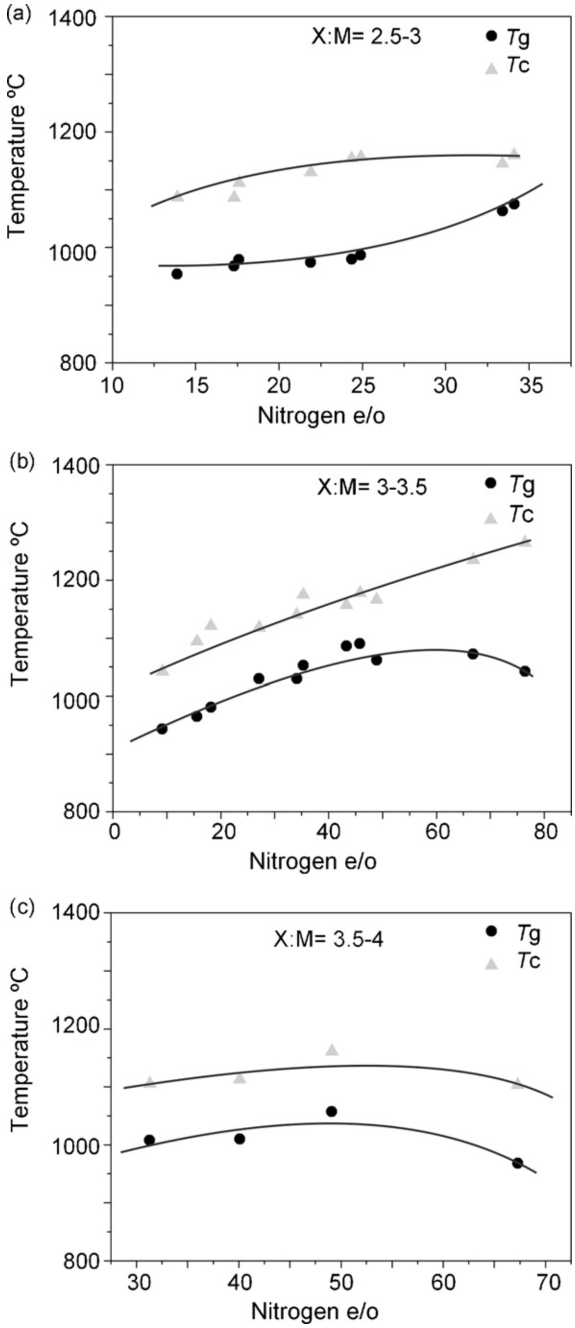

Fig. 6. Glass transition (T_g) and crystallization temperature (T_c) as a function of N content for La–Si–O–N glasses with X:M ratios between (a) 2.5 and 3, (b) 3 and 3.5, and (c) 3.5 and 4. Drawn lines are only for eye guidance.

particles, while in the glasses they were found only with the latter shape. According to the lanthanum–silicon phase diagram,[39] they should melt at temperatures above 1730 °C, which could account for their spherical shape. The amounts of silicides are found to decrease upon increasing the temperature and the holding time, which indicates that they are mostly remnants from the amounts formed early on, and that their amounts could be reduced by using longer holding times. It may also be remarked here that preliminary studies show that, if Al is added as an additional component to the La–Si–O–N system, glasses can be prepared at lower temperatures and in shorter times. These exhibit considerably higher transparencies, and smaller losses of components during preparation.

A comparison of the compositions of the glasses and the starting mixtures shows that primarily Si and N are lost during the heat treatment, with the total loss being ca. 3–7 wt%. The losses were found to increase with increasing temperature and, to a smaller extent, with holding time. They might be due the decomposition reaction proposed by Messier and Deguire,[34] whereby Si departs as gaseous SiO. The reaction implies, however, the formation of elemental Si, whereas, the glasses contain only very minute amounts of elemental Si.

The structures of Si based oxynitride glasses are, in analogy with ordinary oxide glasses, envisaged as essentially consisting of a framework of polymerised $SiO_{4-x}N_x$ ($x = 0$–4) tetrahedra with inter-dispersed modifier cations.[40] The compositions of the prepared La–Si–O–N glasses are thus remarkable in that anion content per Si atom is high, *i.e.* the X:M ratios are high, implying evidently that the tetrahedral frameworks are very fragmented. For example, an X:M ratio of 3 implies that the average connectivity of the framework corresponds to that of rings or strings of tetrahedra, with each tetrahedron having two linking anions and two apex anions. Some insight about the possible structures of the glasses may be gained by comparison with crystalline structures of similar compositions. In Table 2, the

Table 2
Cross-linking of SiX_4 tetrahedra (X = O, N) and connectivity of N for crystalline La–Si–O–N compounds

Compound	Cross-linking of SiX_4 tetrahedra	$X^{[1]}$	$X^{[2]}$	$X^{[3]}$
$La_5(SiO_4)_3N$[41,43,46]	SiX_4 monomers: X:M = 4.33; 11.1 e/o N 55.6 e/o La	Yes	No	No
$La_4Si_2O_7N_2$[41,43,46]	Si_2X_7 dimers: X:M = 4.50; 30.0 e/o N 60.0 e/o La	Yes	Yes	No
$LaSiO_2N$[38,41,43,46]	Si_3X_9 rings; X:M = 3.00; 42.9 e/o N 42.9 e/o La	Yes	Yes	No
$La_3Si_8O_4N_{11}$[41,42,44,45]	$(Si_8X_{15})_n$ network X:M = 1.87; 80.5 e/o N 22.0 e/o La	Yes	Yes	Yes

cross-linking of SiX_4-tetrahedra and connectivity of N are listed for known crystalline La–Si–O–N compounds, together with their cation and anion compositions in e/o. With increasing N:O ratio, the Si frameworks are observed to condense, from consisting of isolated SiO_3N or SiO_4 tetrahedra in $La_5(SiO_4)_3N$, dimeric $Si_2O_5N_2$ units in $La_4Si_2O_7N_2$, trimeric $Si_3O_6N_3$ rings in $LaSiO_2N$, and a three-dimensional $(Si_8O_4N_{11})_n$ network for $La_3Si_8O_4N_{11}$. Concurrently there is an increase in the average connectivity of N and a decrease in the X:M ratios. However, the compositional trends clearly differ between these crystalline compounds and the glasses, which make further comparisons difficult. For the former, the La contents decrease with increasing N concentration, or stated alternatively, the frameworks condense as the nitrogen content increases. This is not observed for the glasses, for which the average connectivity is, broadly speaking, *independent of the anion composition*.

The increase in elastic modulus and hardness with increasing N content for oxynitride glasses has often been attributed to the existence of $N^{[3]}$, effecting an increased cross-linking of the framework and thereby a stiffening of the glass.[40] For the present glasses, which contain far more nitrogen than previously reported ones, the X:M ratios directly imply that the fraction of $N^{[3]}$ is not large. A recent investigation by us of a series of these glasses by solid state NMR[47] indicates accordingly, that for glasses with high X:M ratios, the O and N atoms play similar structural roles, *i.e.* a predominant fraction of the nitrogen atoms are present as $N^{[1]}$ and $N^{[2]}$. It may be noted that anomalously high X:M ratios could be a result of the glasses containing significant amounts of isolated $X^{[0]}$ species, *i.e.* anions not bonded to Si. The NMR data, however, do not support this possibility.

Evidently, further studies are necessary in order to understand the structures of the high-nitrogen content glasses and how properties like *e.g.* hardness vary with composition. It is reasonable to expect that properties are not only dependent on fundamental variables like N content, but also depend on the X:M ratio, as indicated by the observed variation of glass transition temperature.

4. Conclusions

Si based oxynitride glasses have been prepared by a novel route, by heat-treating mixtures of La metal and Si_3N_4 and SiO_2 powders in a nitrogen atmosphere at 1650–1800 °C. The formation of glasses in the La–Si–O–N system is found to depend strongly on the precursors used. The glass forming region is found to be significantly larger than indicated by previous reports. The formation of the glasses proceeds via a strong exothermal reaction at 900–1100 °C, whereby amorphous and crystalline phases are formed, which melt upon further heating. Most glasses contained minor amounts of La silicides, which are probably responsible for the colouring of the glasses. The anion content per Si atom is high for the glasses, ranging from 2.5 to 4, indicating that their structures are unlike those of previously reported glasses with smaller N contents.

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