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La-Si-O-N glasses
Part II: Vickers hardness and refractive index

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Abstract

Vickers hardness and refractive index have been determined for a series of La-Si-O-N oxy-nitride glasses containing 30–62 e/o of La and 9–68 e/o of N. The hardness varies between 7.7 and 11.5 GPa at a load of 1 kg and is dependent of the N content, while the La content does not influence it significantly. The increase of the hardness with N content is, contrary to reported findings for other oxy-nitride glasses, found not to be linear over the whole compositional range. The refractive index varies between 1.8 and 2.3 and increases non-linearly with increasing N content. The compositional variations of hardness and refractive index are compared with previously published results.

Keywords: Oxynitride; Glass; Lanthanum; Hardness; Optical properties

1. Introduction

Glass forming regions and properties of oxy-nitride glasses[1–5] have been studied chiefly because they occur as grain-boundary phases in silicon nitride ceramics, in which the composition and volume fraction of them determine the properties of the materials, particularly the high-temperature mechanical properties. The studies have shown that a number of physical and mechanical property values, including hardness, fracture toughness, elastic modulus and refractive index, increase with increasing nitrogen content. Sakka[2] has emphasized that oxy-nitride glasses exhibit very high elastic moduli, which cannot be achieved by any pure oxide glasses. The values have been found to vary linearly with N content, density of the glass and ionic radius of rare-earth (RE) glass modifier/dopant, with the effects of N and RE contents being independent and additive.[6,7]

Studies of compositional dependencies of hardness are predominant for glasses containing, in addition to Si, Y and Al,[1,2,8–12] and RE and Al,[5,13–15] with the latter mainly concerning variations with the ionic radius and/or cationic strength of the RE cations. Glasses with Mg and RE have also been investigated.[16] Considerably fewer studies have been done on M-Si-O-N systems that contain only Si and one modifier.[17,18] The observed increase in hardness with increasing N content has commonly, but not without exceptions, been attributed to the existence of substantial amounts of $N^{[3]}$, *i.e.* N atoms that bind to three Si atoms, which allegedly increases the cross-linking in the framework and stiffens the glass.[10,18]

Compositional variations of the refractive index have been considerably less investigated than those of mechanical properties. Systems that have been investigated are Y-Al-Si-O-N,[19] M-Si-Al-O-N with M = Mg, Ca, Y, and Nd,[20] RE-Al-Si-O-N[5] and Gd-Al-Si-O-N.[13] The refractive index is found to increase both with increasing N content and, to a substantially smaller extent, with increasing content of glass modifiers of high atomic numbers. Coon et al.[19] found that for Y-Al-Si-O-N glasses an estimated value of the molar refractivity of nitrogen is similar to that predicted for nitrogen in silicon nitride, suggesting that the glasses contain appreciable amounts of $N^{[3]}$.

Silicon oxy-nitride glasses have traditionally been synthesized by melting mixtures of Si_3N_4, SiO_2 and glass modifier metal oxides, yielding glasses with nitrogen contents up to, typically, *ca.* 20 e/o. By using a recently developed alternative synthesis route, in which the electropositive elements are used in the form of metals that convert to nitrides by reaction

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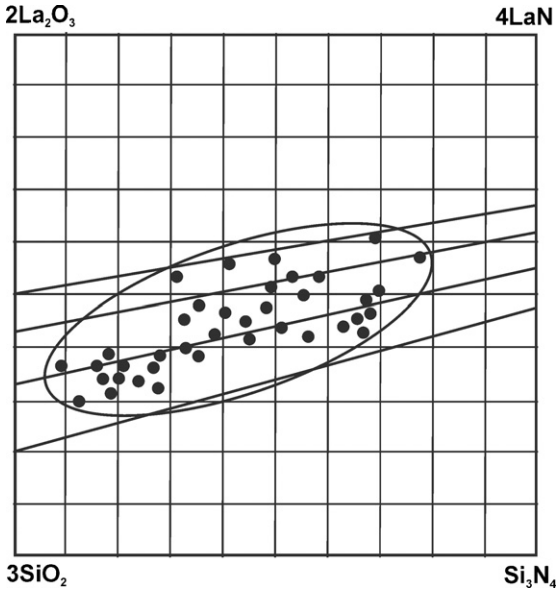

Fig. 1. Glasses obtained in the La_2O_3-SiO_2-LaN-Si_3N_4 system. The slanting lines show selected constant values for the ratio X:M = [O,N]/[Si] of, from bottom up, 2.5, 3.0, 3.5 and 4.0, respectively.

with the nitrogen gas atmosphere, we have prepared a range of oxy-nitride glasses that contain significantly higher contents of both nitrogen and additives.[21] The synthesis and determined glass forming region for La-Si-O-N glasses have been reported elsewhere.[22] Achieved glass compositions are shown in Fig. 1. The glasses were all non-transparent with a dark brown colour. They were characterized by elemental anion and cation analyses, optical and scanning electron microscopy, differential thermal analysis, powder X-ray diffraction and density measurements. The majority of them were found to contain small amounts of La silicides, typically around 1%, and also, by transmission electron microscopy, to a much smaller degree, elemental Si. The present work comprises determinations of Vickers hardness and refractivity index for a series of these La-Si-O-N glasses, some of them containing very high amounts of La and N,[22] together with a comparison of the observed compositional dependencies with previously published data. Data for the glasses are given in Table 1.

2. Experimental

The La-Si-O-N glasses were prepared from powder mixtures of La metal (ChemPure, 99.9%), Si_3N_4 (UBE, SNE10), and SiO_2 (Aerosil 50). The mixtures were melted at 1650–1800 °C, depending on the composition, using a radio frequency furnace. Further information on synthesis conditions and characterization of the obtained glasses is given in Ref. 22.

Hardness was determined using a Vickers hardness testing machine, with a pyramidal diamond indenter and a load (P) of 1 kg, and using the average of five indentions per specimen. In order to reduce strains in the samples, they were heated, prior to the measurements, in a nitrogen atmosphere, to 800 °C

Table 1
Data for La-Si-O-N glasses: determined glass compositions, La cation content in e/o, N content in e/o, the ratio X:M = [O,N]/[Si], Vickers hardness (H_V), refractive index (n), density (ρ)

Composition	La (e/o)	N (e/o)	X:M	H_V (GPa)	n	ρ (g/cm^3)
$La_{5.81}Si_{10}O_{24.22}N_{2.99}$	30.3 (5)	13.9 (4)	2.72	7.8 (2)	1.73	4.24
$La_{8.14}Si_{10}O_{29.164}N_{2.03}$	37.8 (6)	9.2 (3)	3.12	7.7 (2)	1.75	4.48
$La_{7.62}Si_{10}O_{25.57}N_{3.90}$	36.3 (4)	17.6 (2)	2.95	8.7 (2)	1.78	4.70
$La_{7.90}Si_{10}O_{26.56}N_{3.53}$	37.2 (5)	15.6 (7)	3.01	8.6 (2)	1.77	4.44
$La_{8.15}Si_{10}O_{25.93}N_{4.19}$	37.9 (8)	18.2 (3)	3.01	9.3 (3)	1.80	4.55
$La_{7.84}Si_{10}O_{26.17}N_{3.73}$	37.1 (3)	17.3 (6)	2.99	9.1 (3)	1.79	4.69
$La_{7.06}Si_{10}O_{22.27}N_{5.55}$	34.6 (6)	24.9 (4)	2.78	9.4 (2)	1.84	4.44
$La_{7.45}Si_{10}O_{23.59}N_{5.05}$	35.8 (6)	21.9 (3)	2.86	9.4 (2)	1.84	4.56
$La_{7.59}Si_{10}O_{22.95}N_{5.62}$	36.2 (3)	24.4 (6)	2.86	9.6 (2)	1.87	4.66
$La_{12.22}Si_{10}O_{24.01}N_{9.55}$	47.8 (5)	35.3 (3)	3.36	10.3 (3)	1.92	5.15
$La_{8.52}Si_{10}O_{23.25}N_{6.36}$	38.9 (6)	27.1 (7)	2.96	9.9 (2)	1.88	4.72
$La_{8.25}Si_{10}O_{20.28}N_{8.06}$	38.2 (5)	34.1 (3)	2.83	10.2 (4)	1.89	4.68
$La_{8.82}Si_{10}O_{20.89}N_{8.22}$	39.8 (3)	33.4 (4)	2.91	10.6 (3)	1.89	4.77
$La_{16.1}Si_{10}O_{29.68}N_{9.62}$	54.6 (7)	31.3 (5)	3.93	10.6 (2)	1.94	5.46
$La_{16.45}Si_{10}O_{26.24}N_{12.28}$	55.2 (5)	40.1 (4)	3.85	10.7 (2)	1.95	5.42
$La_{11.62}Si_{10}O_{23.89}N_{9.03}$	46.5 (8)	34.1 (3)	3.29	9.4 (3)	1.92	5.14
$La_{13.4}Si_{10}O_{16.78}N_{15.54}$	50.1 (8)	56.9 (3)	3.23	11.3 (2)	1.95	–
$La_{11.03}Si_{10}O_{20.42}N_{10.75}$	45.2 (4)	43.3 (8)	3.12	10.4 (2)	1.94	4.91
$La_{14.62}Si_{10}O_{18.4}N_{15.67}$	52.2 (3)	58.3 (6)	3.41	11.3 (3)	1.96	5.27
$La_{12.04}Si_{10}O_{19.7}N_{12.24}$	47.4 (4)	45.8 (7)	3.19	10.8 (4)	1.94	5.28
$La_{18.15}Si_{10}O_{23.02}N_{16.13}$	57.6 (5)	49.1 (3)	3.92	10.9 (2)	1.98	5.51
$La_{11.7}Si_{10}O_{11.53}N_{17.34}$	46.7 (3)	65.7 (4)	2.89	11.4 (2)	2.17	–
$La_{10.64}Si_{10}O_{12.92}N_{15.36}$	44.3 (4)	62.6 (5)	2.83	11.3 (2)	2.06	–
$La_{12.33}Si_{10}O_{9.42}N_{19.38}$	48.1 (4)	67.9 (5)	2.88	11.5 (2)	2.20	–
$La_{13.1}Si_{10}O_{12.57}N_{18.23}$	49.4 (6)	66.8 (3)	3.05	11.4 (2)	2.31	4.99
$La_{14.04}Si_{10}O_{19.39}N_{14.5}$	51.3 (3)	48.9 (6)	3.39	11.3 (2)	1.94	5.36
$La_{21.72}Si_{10}O_{10.11}N_{28.32}$	61.9 (5)	67.3 (3)	3.84	11.5 (3)	2.28	5.51

Numbers in parentheses are estimated standard deviations.

at a rate of 5° min^{-1} and then cooled at a rate of 2° min^{-1}. The variation of obtained hardness values with indentation load was investigated on a smaller set of samples, using in addition a Matsuzawa microhardness tester, Model MXT-α1. The indentation diagonal lengths (d) were measured using an optical microscope, Vickers hardness values were calculated using the expression $H_V = (1854\,\text{kgf}\,\mu\text{m}^2/\text{gf}\,\text{mm}^2)\,P/d^2$ and then converted to SI units.

The refractive index was determined using an in-house built apparatus for measuring the Brewster angle, θ_B,[23] with a laser light source operating at $\lambda = 633$ nm, and calculating the refractive index n from $n = \tan(\theta_B)$. The samples were mounted in bakelite for the measurements, and their surfaces were finely polished with 4000 mesh SiC paper then with fine fabrics of 20, 6, 1 μm, respectively. The precision of the measurement of n was estimated to be 0.03 on the average, corresponding to an error of *ca.* 1° in $2\theta_B$.

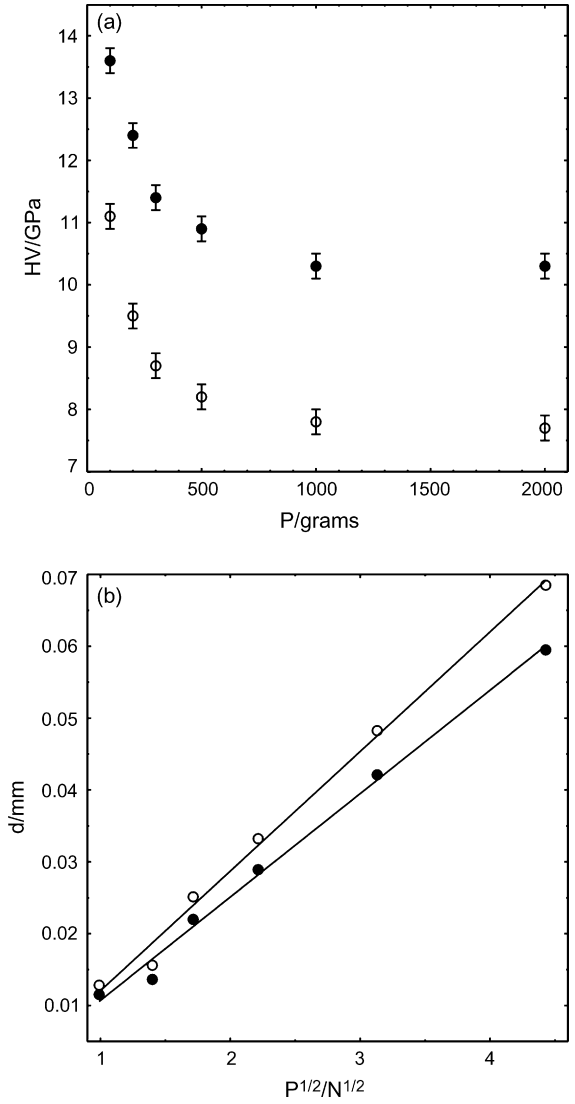

Fig. 2. (a) Hardness H_V as a function of applied load, P, and (b) diagonal indention length, d, as a function of the square root of the applied load for glasses with compositions $La_{12.22}Si_{10}O_{24.01}N_{9.55}$ (●) and $La_{5.81}Si_{10}O_{24.22}N_{2.99}$ (○).

3. Results

3.1. Vickers hardness

The measurements showed that there was a considerable decrease of the apparent hardness, H_V, with increasing load. In Fig. 2(a) the measured hardness is given as a function of applied load, and in Fig. 2(b) the indention diagonal length d is plotted versus the square root of the load P, for two glasses. According to the Bull equation,[24] the slope of the straight line is $(1.854/H_V^0)^{1/2}$, with H_V^0 the load-independent part of the hardness. The calculated H_V^0 values for the two glasses show that H_V values using a load of 1 kg are relatively close to load-independent values, amounting to *ca.* $1.15H_V^0$, while, *e.g.* a load of 100 g gives apparent hardness values that are substantially higher, *ca.* $(1.5 - 1.7)H_V^0$.

The hardness H_V, at a load of 1 kg, is plotted in Fig. 3 as a function of the nitrogen content [N] in e/o. It increases non-linearly from *ca.* 7.7 GPa for *ca.* 10 e/o of N to *ca.* 11.5 GPa for *ca.* 70 e/o of N. A fit of the data to a second degree polynomial yielded the dependence $H_V = 6.6(3) + 0.14(2)[\text{N}] - 1.0(2) \times 10^{-3}[\text{N}]^2$ with $R = 0.93$ and a standard error of 0.3. The data in the figure are divided into three groups of X:M ((O/N):Si) values. The variable X:M is strongly correlated with the La content, and the data indicate that the hardness is not significantly influenced by either X:M or La content.

3.2. Refractive index

The measured refractive index, n, is plotted versus the N content in Fig. 4. The variation of n with nitrogen content [N] is found to be non-linear. It increases, within error, linearly with nitrogen content up to *ca.* 30 e/o, range A in Fig. 4, but is nearly constant at $n \approx 1.95$ for nitrogen con-

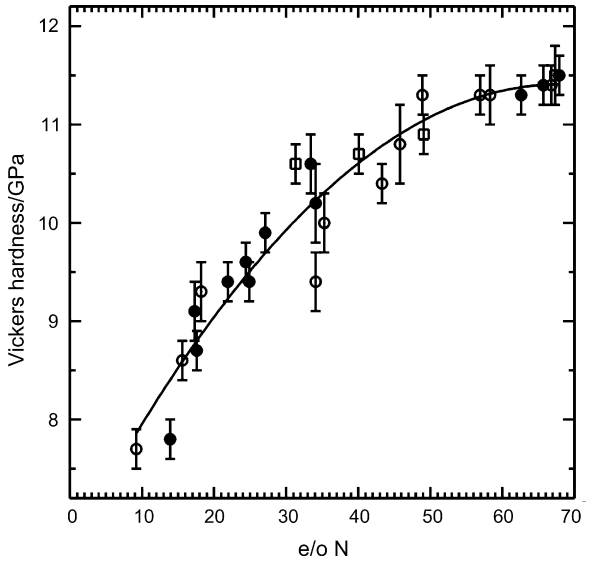

Fig. 3. Vickers hardness, H_V, for La-Si-O-N glasses as a function of nitrogen content. X:M = 2.5–3.0 (●), X:M = 3.0–3.5 (○), X:M = 3.5–4.0 (□).

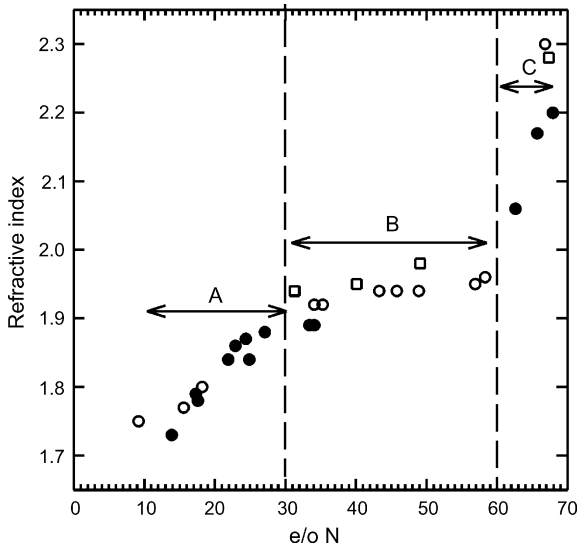

Fig. 4. Refractive index, n, at 633 nm for La-Si-O-N glasses as a function of nitrogen content. X:M = 2.5–3.0 (●), X:M = 3.0–3.5 (◯), X:M = 3.5–4.0 (□).

tents between 40 and 60 e/o, range B. A fit of the data for [N] < 60 e/o to a second degree polynomial (omitting the outlier data point at 9 e/o N) yields the dependence as $n = 1.56(3) + 1.57(2) \times 10^{-2}[\mathrm{N}] - 1.56(2) \times 10^{-4}[\mathrm{N}]^2$ with standard error 0.02 and $R = 0.95$. At higher N contents, between 60 and 68 e/o N, range C, there is a further substantial increase of n with increasing N content, and n reaches a maximum value of *ca.* 2.3 for [N] *ca.* 68 e/o N. The data in Fig. 4 shows that there is also comparatively much smaller, dependence of n on the X:M ratio, implying a small dependence on the La content, in agreement with previous findings.[6,7] Including a linear dependence of n on the La content, [La], in a fit for the data with [N] < 60 e/o yielded the dependence as $n \propto 1.9(2) \times 10^{-3}[\mathrm{La}]$, *i.e.* the dependence on [La] is found to be roughly 10 times less than on [N].

4. Discussion

Comparatively many hardness studies of oxy-nitride glasses are found for the system Y-Si-Al-O-N,[9–12,25,26] reflecting the importance of these glass compositions for Si_3N_4 based ceramics. The Vickers hardness for these glasses varies roughly between 8 and 11.5 GPa for N contents below 33 e/o. Only one study has been made of the system RE-Si-Al-O-N,[14] with RE = Ce–Er, with the hardness increasing from 9 to 11.4 GPa with decreasing size of the RE cation at 17 e/o N. For the present system, La-Si-O-N, literature data are only available for one glass composition with 38 e/o of N,[27] exhibiting a hardness of 11 GPa at a load of 100 g. A comparison of the above results with those in the present study is obstructed by the use of different loads. The conclusions that can be made are: (i) that the present glasses in comparison exhibit high hardness values at high N contents, (ii) that the increase of hardness with N content is not linear over the whole compositional range of 9–68 e/o N, and (iii) that there is no significant influence on the hardness by the X:M ratio or La content.

The increase in hardness with N content for oxy-nitride glasses has predominantly been attributed to an introduction of $N^{[3]}$, which increases the cross-linkage and stiffens the glass. In some studies[15] it has been recognized that the higher bending resistance of Si–$N^{[2]}$–Si linkages,[28] in comparison with Si–$O^{[2]}$–Si linkages, should also effect an increased hardness. However, the X:M ratios for the present glasses imply, especially for those with high N and La contents, that the Si-(O,N) frameworks are very fragmented. Indeed, if the possible presence of O/N atoms not bonded to Si in the glass structures is disregarded, some of the glasses should ostensibly contain predominantly isolated $Si(O/N)_4$ and $Si_2(O/N)_7$ groups. The existence of appreciable amounts of $N^{[3]}$ is for this reason not likely at high N contents. A recent solid-state NMR study of a selected number of these glasses indicates, in accordance, that N and O in fact play similar structural roles.[29] The role of the glass modifier, in this case La, is furthermore frequently overlooked. In Si-Al-Sm-O glasses[30] the hardness increases upon substitution of Sm for Al, and it has been suggested that strong O-Y-O cross-linking bonds contribute to a high hardness in Y-Si-Al-O-N glasses.[10,15] For very high X:M ratios and La contents, the present glasses may be considered as close to inverted, *i.e.* the main matrix being La-(O/N), and the hardness therefore expected to be to a considerable degree also governed by La–O and La–N bonds. Structural studies of these glasses are evidently necessary to shed light on these issues.

The observed non-linear variation of the refractive index with nitrogen content is indicative of changes in glass structure, and thus bonding between different atoms, that take place with increasing nitrogen content over the wide compositional range of 9–68 e/o of N. The structural issues mentioned above in connection with the hardness of the glasses are thus equally valid for a discussion of the refractive index. In present glasses, refractive index (n) was divided into three compositional ranges with respect to: range A (see Fig. 4) with [N] < 30 e/o, where n increases linearly with [N], in accordance with the findings of other studies,[6,19] a range B with [N] between *ca.* 40 and 60 e/o N, where n is fairly constant, and a range C with [N] > 60 e/o, where n increases markedly with N content. In range A most of the glasses have X:M ratios between 2.5 and 3, whereas those in range B have higher X:M ratios, between 3 and 4. It is thus natural to attribute the different dependency on N content in these ranges to differences in framework connectivity, and in particular the connectivity of the N atoms. For Y-Al-Si-O-N glasses with N contents in the range A, the estimated molar refractivity of nitrogen has been taken as indicating that the glasses contain appreciable amounts of $N^{[3]}$.[19] The relative amounts of $N^{[3]}$ in oxy-nitride glasses are, however, quantitatively not known in general. In range B, the X:M ratios imply very fragmented frameworks. The nearly constant n in this range could thus be due to N being predominantly present as $N^{[1]}$ and $N^{[2]}$, in relatively constant proportions. Without structural information, only speculative reasons can be given for the marked increase of n with N content in range C. These glasses all have, in addition to very high N contents, also very high La contents, 44–62 e/o. Speculatively, the high n values might be caused by a segregation at a nanometer scale of La- and Si-rich regions, and also by the boundaries present between these regions.

5. Conclusions

Previous investigations of the variation of hardness and refractive index in oxy-nitride glasses have, with few exceptions, been restricted to N contents up to *ca.* 30 e/o, while in this study La-Si-O-N glasses containing up to 68 e/o of N have been characterized. The increase in hardness with nitrogen content is found to be non-linear. The refractive index increases non-linearly with nitrogen content, and the glasses can be divided into three compositional ranges: (a) with [N] < 30 e/o, where n increases linearly with [N], (b) with [N] between *ca.* 40 and 60 e/o N, where n is fairly constant, and (c) with [N] > 60 e/o, where n increases markedly with N content. The variation of the refractive index indicates that changes in glass structure and bonding between different atoms take place upon varying the nitrogen content over the wide compositional range of 9–68 e/o of N.

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References

1. Loehman, R. E., Oxynitride glasses. *J. Non-Cryst. Solids*, 1980, **42**, 433–445.
2. Sakka, S., Oxynitride glasses. *Ann. Rev. Mater. Sci.*, 1986, **16**, 29–46.
3. Hampshire, S., Oxynitride glasses and glass ceramics. *Mater. Res. Soc. Symp. Proc.*, 1993, **287**, 93–104.
4. Hampshire, S., Oxynitride glasses, their properties and crystallisation—a review. *J. Non-Cryst. Solids*, 2003, **316**, 64–73.
5. Redington, W., Redington, M., Hampshire, S. and Serantoni, M., Properties of some high Al content glasses in various lanthanide-Si-Al-O-N systems. *J. Non-Cryst. Solids*, 2003, **316**, 74–81.
6. Lofaj, F., Satet, R., Hoffmann, M. J. and de Arellano-López, A. R., Thermal expansion and glass transition temperature of the rare-earth doped oxynitride glasses. *J. Eur. Ceram. Soc.*, 2004, **24**, 3377–3385.
7. Pomeroy, M. J., Mulcahy, C. and 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. *J. Am. Ceram. Soc.*, 2003, **86**, 458–464.
8. Sun, E. Y., Becher, P. F., Hwang, S.-L., Waters, S. B., Pharr, G. M. and Tsui, T. Y., Properties of silicon-aluminum-yttrium oxynitride glasses. *J. Non-Cryst. Solids*, 1996, **208**, 162–169.
9. Messier, D. R., Preparation and properties of Y-Si-Al-O-N glasses. *Int. J. High Technol. Ceram.*, 1987, **3**, 33–41.
10. de Graaf, D., Braciszewicz, M., Hintzen, H. T., Sopicka-Lizer, M. and de With, G., The influence of the composition on (the load-dependence of) the microhardness of Y-Si-Al-O-N glasses as measured by Vickers indentation. *J. Mater. Sci.*, 2004, **39**, 2145–2149.
11. Messier, D. R. and Broz, A., Microhardness and elastic moduli of Si-Y-Al-O-N glasses. *Commun. Am. Ceram. Soc.*, 1982, **65**, C-123.
12. Hampshire, S., Drew, R. A. L. and Jack, K. H., Viscosities, glass transition temperatures, and microhardness of Y-Si-Al-O-N glasses. *Commun. Am. Ceram. Soc.*, 1984, **67**, C46–C47.
13. Rocherulle, J., Verdier, P. and Laurent, Y., Preparation and properties of gadolinium oxide and oxynitride glasses. *Mater. Sci. Eng.*, 1989, **B2**, 265–268.
14. Ramesh, R., Nestor, E., Pomeroy, M. J. and Hampshire, S., Formation of Ln-Si-Al-O-N glasses and their properties. *J. Eur. Ceram. Soc.*, 1997, **17**, 1933–1939.
15. Becher, P. F., Waters, S. B., Westmoreland, C. G. and Riester, L., Compositional effects on the properties of Si-Al-RE-based oxynitride glasses (RE = La, Nd, Gd, Y, or Lu). *J. Am. Ceram. Soc.*, 2002, **85**(4), 897–902.
16. Lofaj, F., Hvizdos, P., Dorčáková, F., Satet, R., Hoffmann, M. J. and de Arellano-López, A. R., Indentation moduli and microhardness of RE-Si-Mg-O-N glasses (RE = Sc, Y, La, Sm, Yb and Lu) with different nitrogen content. *Mater. Sci. Eng.*, 2003, **A357**, 181–187.
17. Coon, D. N., Rapp, J. C., Bradt, R. C. and Pantano, C. G., Mechanical properties of silicon-oxynitride glasses. *J. Non-Cryst. Sol.*, 1983, **56**(1–3), 161–166.
18. Ohashi, M., Nakamura, K., Hirao, K., Kanzaki, S. and Hampshire, S., Formation and properties of Ln-Si-O-N glasses (Ln: lanthanides or Y). *J. Am. Ceram. Soc.*, 1995, **78**, 71–76.
19. Coon, D. N., Doyle, T. E. and Weidner, J. R., Refractive indices of glasses in the Y-Al-Si-O-N system. *J. Non-Cryst. Solids*, 1989, **108**, 180–186.
20. Drew, R. A. L., Hampshire, S. and Jack, K. H., The preparation and properties of oxynitride glasses. In *Progress in nitrogen ceramics*, ed. F. L. Riley. Martinus Nijhoff Publishers, The Hague, 1983, pp. 323–330.
21. Hakeem, A. S., Daucé, R., Leonova, E., Edén, M., Shen, Z., Grins, J. and Esmaeilzadeh, S., Silicate glasses with unprecedented high nitrogen and electropositive metal contents obtained by using metals as precursors. *Adv. Mater.*, 2005, **17**, 2214–2216.
22. Hakeem, A. S., Grins, J., Esmaeilzadeh, S., La-Si-O-N glasses, Part I. Extension of the glass forming region, *J. Eur. Cerm. Soc.*, submitted for publication.
23. Luna-Moreno, D., De la Rosa-Cruz, E., Cuevas, F. J., Regaldo, L. E., Salas, P., Rodríguez, R. and Castaño, V. M., *Opt. Mater.*, 2002, **19**, 275–281.
24. Bull, S. J., Page, T. F. and Yoffe, E. H., An explanation of the indentation size effect in ceramics. *Philos. Mag. Lett.*, 1989, **59**, 281–288.
25. Loehman, R. E., Preparation and properties of yttrium-silicon-aluminium oxynitride glasses. *J. Am. Ceram. Soc.*, 1979, **62**, 491–494.
26. Lemercier, H., Rouxel, T., Fargeot, D. and Besson, B. P., Yttrium SiAlON glasses: structure and mechanical properties, elasticity and viscosity. *J. Non-Cryst. Solids*, 1996, **201**, 128–145.
27. Makishima, A., Mitomo, M., Tanaka, H., Ii, N. and Tsutsumi, M., Microhardness and transparency of an La-Si-O-N oxynitride glass. *J. Am. Ceram. Soc.*, 1983, **66**, C55–C56.
28. Sakka, S., Structure, properties and application of oxynitride glasses. *J. Non-Cryst. Solids*, 1995, **181**, 215–224.
29. Leonova, E., Hakeem, A. S., Jansson K., Kaikkonen, A., Shen, Z., Grins, J., Esmaeilzadeh, S., Edén, M., Nitrogen-rich La-Si-Al-O-N oxynitride glass structures probed by solid state NMR, *J. Non-Cryst. Solids*, submitted for publication.
30. Erbe, E. M. and Day, D. E., Properties of Sm_2O_3-Al_2O_3-SiO_2 glasses for in vivo applications. *J. Am. Ceram. Soc.*, 1990, **73**, 2708–2713.