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Structural characterisation of Er–Si–Al–O–N glasses by Raman spectroscopy

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Abstract

Er–Si–Al–O–N glasses have been prepared with cation ratio Er:Si:Al = 3.45:3:2 containing various amounts of nitrogen (N = 0, 5, 8, 15 and 22 equiv.%). Glass properties such as microhardness, glass transition temperature and dilatometric softening temperature were measured and it was found that these properties increased linearly with increasing nitrogen content. Glasses were then characterised using Raman spectroscopy in order to obtain information about the structure of these glasses. Deconvolution of peaks in the Raman spectra of Er–Si–Al–O–N glasses revealed that, as nitrogen content increases then the proportion of Q^3 species decreases and there is a corresponding increase in the proportion of Q^4 species (Q^n: n = no. of bridging anions joining SiO_4 tetrahedra), confirming that nitrogen increases the crosslinking between individual tetrahedra via the transformation of Q^3 oxide species into Q^4 oxynitride species.

Keyword: Raman spectroscopy

1. Introduction

Oxynitride glasses are silicate or alumino-silicate glasses in which oxygen atoms in the glass network are partially replaced by nitrogen atoms.[1] They are important because they exist as glass phases at grain boundaries in silicon nitride and SiAlON ceramics as a result of the use of oxide sintering additives. The compositions and volume fractions of these glass phases determine the properties of the ceramics, particularly their high temperature mechanical behaviour.[2–4]

A number of investigations have been carried out on bulk glass formation and properties in several M–Si–O–N and M–Si–Al–O–N systems where M is a modifying cation such as the alkaline earths (Mg, Ca, Ba)[5–9] or Y[5–7,10–15] and the rare earth lanthanides.[16–24] The first systematic studies[5,6,11] on the effect of replacing oxygen by nitrogen in oxynitride glasses reported that for all Mg–, Ca–, Y– and Nd–Si–Al–O–N glasses with constant cation ratios, incorporation of nitrogen resulted in increases in glass transition temperature (T_g), viscosity, hardness, refractive index, dielectric constant and ac conductivity. Viscosity increases by more than two orders of magnitude simply by replacing 18 e/o oxygen by nitrogen.[1,4] A later extensive study of the Y–Si–Al–O–N system[14] confirmed that T_g, viscosity, microhardness, Young's and shear moduli all increase systematically with increasing nitrogen:oxygen ratio for different series of glasses with fixed cation compositions. More recently,[23] the structure and properties of RE–Mg–Si–O–N glasses have been correlated.

The resulting improvements in glass properties by substitution of nitrogen for oxygen have usually been attributed to an increase in the cross-linking of the silicate network due to the replacement of a two-coordinated bridging oxygen atom, by a bridging nitrogen atom coordinated by three silicon ions. Studies on the coordination of nitrogen in oxynitride glasses using Fourier transform infrared spectroscopy (FT-IR),[26] nuclear magnetic resonance (NMR),[18,27] neutron diffraction[18,28] and Raman spectroscopy[29] have been carried out. The structural features are as follows:

(1) Nitrogen is present in the structural network as Si–N bonds, as shown from FT-IR by the shifting of the position of the Si–O–Si stretching peak towards that of Si–N. If nitrogen exists only as precipitated Si_3N_4, the position of the Si–O–Si peak would not be expected to change. The preference is for Si–N bonding over Al–N as indicated by ^{29}Si NMR.[18]

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(2) Nitrogen is present in three-fold coordination (suggested by XPS studies and this is consistent with systematic changes in the physical and chemical properties of the glasses). However, some nitrogen atoms are bonded to only two Si atoms, or even one, instead of three, as in:
(a) $\equiv$Si–N$^-$–Si$\equiv$
(b) $\equiv$Si–N^{2-}
This suggests that non-bridging nitrogen atoms may also be present. The local charge on the non-bridging nitrogen ions is balanced by the presence of interstitial metal ions ("network dwelling" ions) in their vicinity. In the case of silicate glasses, non-bridging oxygen atoms replace bridging oxygen atoms at high modifier contents. For (a) above, while the N atom links two silicon atoms rather than three, it is still effectively a "bridging" ion.
(3) The glass network contains SiO_4, SiO_3N and SiO_2N_2 tetrahedral structural groups identified by ^{29}Si NMR–MAS.[18]

The current investigation was undertaken in order to determine structural features of certain Er–Si–Al–O–N glasses with constant cation compositions but varying nitrogen contents and to correlate these with changes in properties of the glasses.

2. Experimental procedure

M–Si–Al–O–N glass compositions with cation ratios M:Si:Al = 3.45:3:2 (M = Er) and with varying nitrogen contents (0, 5, 8, 15 and 22 equiv.% N) were prepared from mixtures of high purity (better than 99.9%) powders of Si_3N_4 (UBE), SiO_2 (Fluka Chemika), Al_2O_3 (Aldrich Chemicals) and Er_2O_3 (Rare Earth Chemicals). When calculating the compositions, the 1.28% oxygen present on the surface of Si_3N_4 as surface silica was taken into account. Following calcining and weighing, the powders were mixed by ball milling under isopropanol using sialon milling media for 16 h. Ball milled powders were then dried by evaporation in a rotovap. The dried powders were pressed into compacts by cold isostatic pressing at 150 MPa. These were then placed in a boron nitride lined graphite crucible and melted at 1715 °C in a vertical tube furnace under flowing nitrogen at 0.1 MPa for 1 h. The melt was then quickly removed and poured into a pre-heated graphite mould followed by annealing at 900 °C for 1 h and then slow cooling to room temperature.

Specimens were cut from the glass billets using a diamond saw. The densities were measured using an Archimedes technique. Specimens of the glass were then mounted in a cold setting resin, polished to a 1 μm finish and then subjected to microhardness testing (Leco microhardness tester) using a 100 g load applied for 15 s. Glass transition and dilatometric softening temperatures were measured for a heating rate of 10 °C min^{-1}, using a Netch dilatometer.

Raman Spectroscopy was conducted on a DILOR XY Labram instrument using a He–Ne 20 mW laser under a tension of 7.54 mA through a number of 1800 grating and the generated spectra were collected with a Peltier cooled CCD detector. An excitation source of wavelength 514.5 nm was used. Raman focusing and imaging was conducted using a confocal microscope (Olympus BX40) with an objective of 100×. Other operation parameters applied were a pinhole of 400 mm, a slit opening of 150 mm, an accumulation time of 120 s and an accumulation number of 10. The sample employed was a highly polished 1.2 mm thick slice of the glass. A commercially available peak fitting module in the ORIGIN PRO 7.5 software package was used to deconvolute specific parts of interest of the Raman spectra obtained for each of the different glasses.

3. Results and discussion

Table 1 gives selected properties and colour of the Er–Si–Al–O–N glasses containing 5, 8, 15 and 22 equiv.% nitrogen. All glasses were XRD amorphous and backscattered scanning electron microscopy showed them to be chemically homogeneous. Their wine-pink colour was characteristic of the erbium dopant. It is seen from Table 1 that density increases with increasing nitrogen content and this is solely attributable to the fact that nitrogen causes increases in glass compactness as noted previously.[30] From Table 1 it is also clear that microhardness, glass transition temperature and dilatometric softening temperature increase with increasing nitrogen content. Figs. 1 and 2 indicate a linear correlation between increases in these three properties and nitrogen content. Given that previous research has confirmed linear trends between property values and nitrogen content when the cation ratio is fixed,[4,11,30] then the linearity indicated in Figs. 1 and 2 is valid. Table 2 gives least squares fit equations for each property as well as standard error values which are similar to those expected from the experimental techniques. The slopes of the correlations are in reasonable agreement with previously published data for Mg–Y–Si–Al–O–N glasses[30] indicating that the property enhancement afforded by nitrogen substitution for oxygen is independent of cation composition.

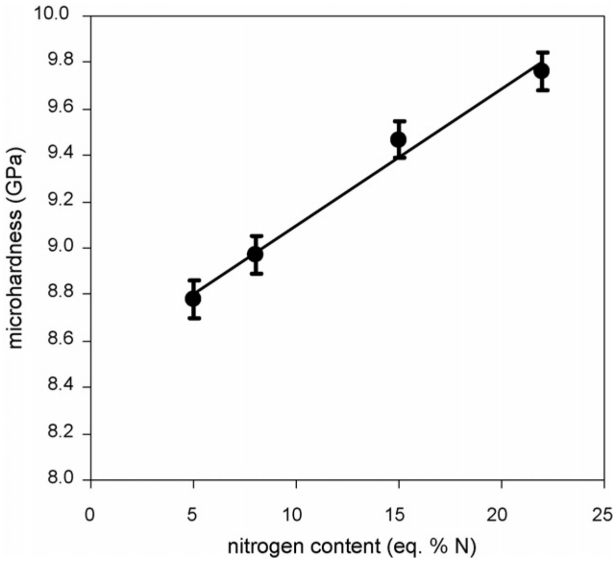


Fig. 1. Effect of nitrogen content on microhardness for Er–Si–Al–O–N glasses (constant 3.45Er:3Si:2Al ratio).

Table 1
Effect of nitrogen content on properties of Er–Si–Al–O–N glasses (Er:Si:Al = 3.45:3:2)

Nitrogen content (equiv.% N)	Colour	Density (g cm^{-3})	Mean microhardness (GPa)	T_g (°C)	T_{DS} (°C)
5	Wine pink	5.68	8.78	845	899
8	Wine pink	5.70	8.97	853	914
15	Wine pink	5.74	9.47	865	919
22	Wine pink	5.83	9.76	897	943

T_g: glass transition temperature; T_{DS}: dilatometric softening temperature.

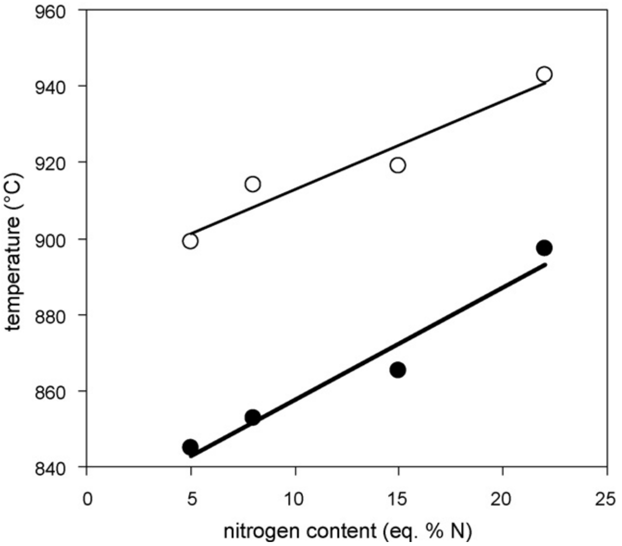


Fig. 2. Effect of nitrogen content on glass transition temperature (open symbols) and dilatometric softening temperature (filled symbols) for Er–Si–Al–O–N glasses.

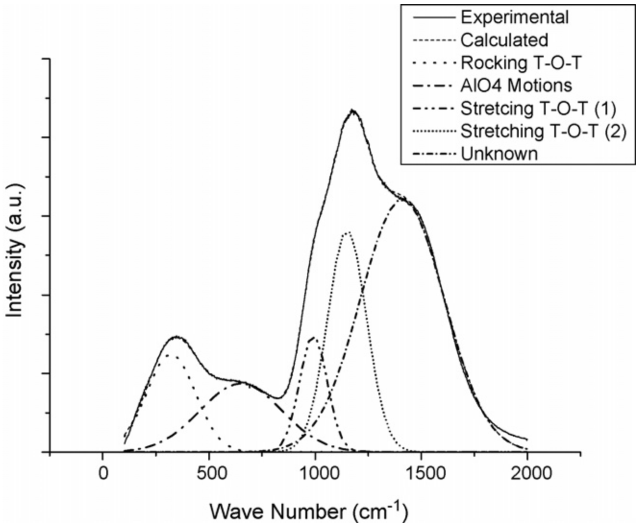


Fig. 3. Raman spectrum for 0 equiv.% Er–Si–Al–O–N glass.

The accepted argument as to why nitrogen enhances property values involves the greater crosslinking effect of tri-coordinated nitrogen compared to the bi-coordinated oxygen it replaces.[1,6,7,26,29] Accordingly, the glass network becomes more crosslinked, with consequent increases in microhardness with N, and also increases in the temperatures at which segmental motion (T_g) or relative motion (T_{DS}) can begin to occur. It has been shown[31–33] that nitrogen is partitioned between SiO_3N and SiO_2N_2 tetrahedra with the major part being in the former tetrahedron type.

Raman spectroscopy of the glasses shows clear structural information due to the Raman activity of erbium. Data for a 0 equiv.% N glass is given in Fig. 3, together with the types of bonds the deconvoluted peaks could be ascribed to. Peak identification was based upon data from the literature.[29,34] In order to facilitate more detailed analysis, relative peak areas for certain bond types were evaluated. It was, however, impossible to find the identity of the peak centred around 1450 cm^{-1}. It is assumed to arise from an Er-related effect and this has been observed to some extent from experiments with Ca–Si–Al–O–N glasses where the peak at 1450 cm^{-1} becomes prominent when Ca was substituted by Er. The intensity of this peak is observed from Fig. 4 to increase slightly with nitrogen content. Fig. 4 also shows that the relative peak areas for the Al(IV)–O motions associated with Al–O network bonds is unaffected by nitrogen content which might be expected given that there is a 3.45Er:2Al ratio which is more than sufficient to ensure the charge balancing of $(AlO_4)^{5-}$ tetrahedra, given that each $(AlO_4)^{5-}$ requires only 1/3Er^{3+} to effect this. This might also be expected since nitrogen preferentially bonds to silicon and thus would not be expected to interfere with the local Al–O structure. Based upon

Table 2
Linear correlations for microhardness, T_g and T_{DS} as a function of nitrogen content for Er–Si–Al–O–N glasses

Microhardness (GPa) = 8.51 + 0.06 × equiv.% N ± 0.06
T_g (°C) = 828 + 2.96 × equiv.% N ± 6.0
T_{DS} (°C) = 890 + 2.32 × equiv.% N ± 6.1

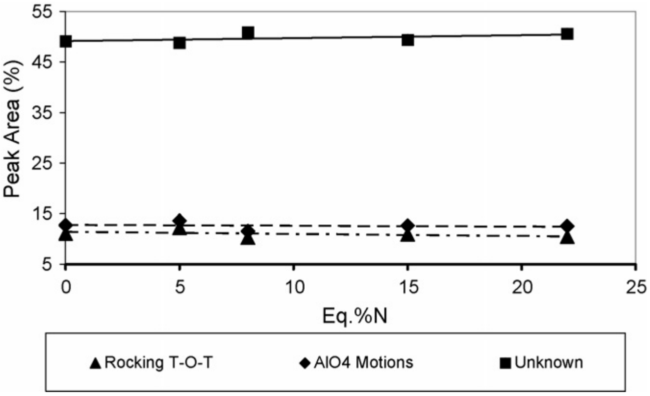


Fig. 4. Effect of nitrogen content on percentage area under peaks for rocking T–O–T, AlO_4 motions and unknown for Er–Si–Al–O–N glasses.

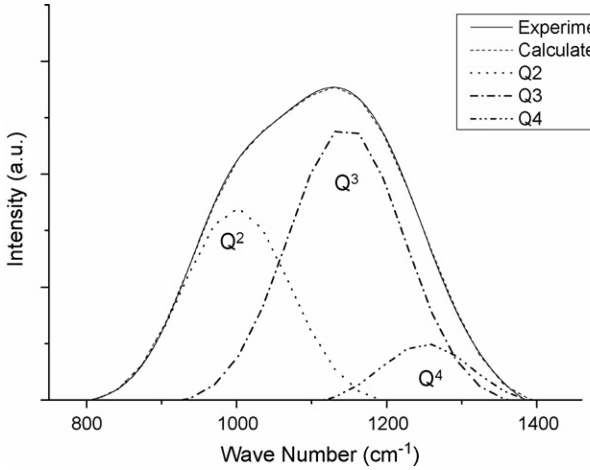


Fig. 5. Typical deconvolution result for main Si–O peak in Raman Spectrum of Er–Si–Al–O–N glass.

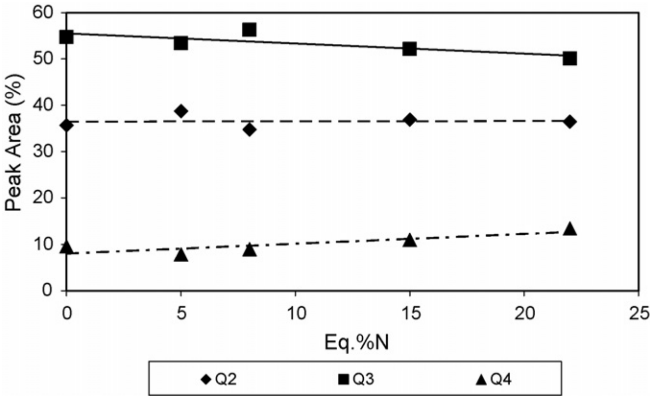


Fig. 6. Effect of nitrogen content on percentage area under peaks for Q^2–Q^4 species in Er–Si–Al–O–N glasses.

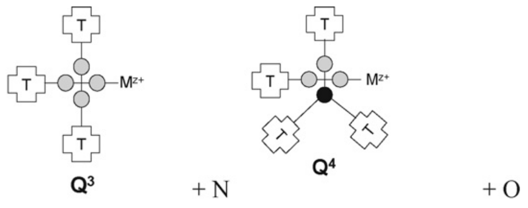
these arguments it is concluded that all Al is tetrahedrally coordinated in these Er–Si–Al–O–N glasses. For the T–O–T rocking linkages, it is seen from Fig. 4 that there is an apparent decrease in their intensity with increasing nitrogen. This is most probably due to the increase in the intensity of the unknown peak.

The broad peak in the wavenumber range 800–1400 cm^{-1} has been ascribed to Si–O symmetric bonds associated with network Si–O–Si bridges.[34–37] This broad ranging peak was stripped out of the Raman spectrum and deconvoluted on the basis of a previously known method[34] for determination of the proportions of Q^2–Q^4 structural units in sodium silicate glasses which was verified by comparison with MAS–NMR data.[38]

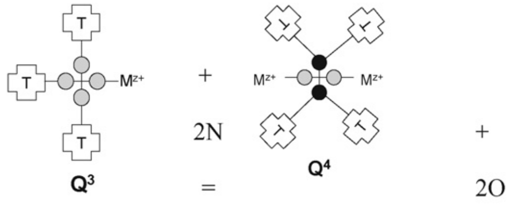
Prior to deconvolution, however, it was necessary to consider the various possible Q units which could arise in a nitrogen substituted glass. In the case of the SiO_2N_2 tetrahedron, it could be co-ordinated to a maximum of six adjacent tetrahedra in the network, two via oxygen linkages and four via nitrogen linkages, giving a Q^6 designation. A Q^5 designation is appropriate for the SiO_3N tetrahedron, since it could be bonded to three adjacent network tetrahedra via oxygen linkages and two others via the nitrogen atom. Accordingly, once all other peaks (excepting that covering the 800–1400 cm^{-1} range) had been stripped from the Raman spectrum, Origin PRO deconvolution routines were run for five possible peaks (Q^2–Q^6), four possible peaks (Q^2–Q^5) and three possible peaks (Q^2–Q^4). It became clear that the best fit for the data for each of the glasses was a deconvolution for three peaks corresponding to Q^2–Q^4, as Fig. 5 shows. Based on this deconvolution routine, relative peak areas were obtained for the three Q values and these are plotted as a function of nitrogen content in Fig. 6. Fig. 6 shows that as nitrogen content increases, then the proportion of Q^3 species decreases and there is a corresponding increase in the proportion of Q^4 species. The proportion of Q^2 species is seen to be independent of nitrogen content. This therefore implies that a reaction of the type $Q^3_{\mathrm{O}} + \mathrm{N} = Q^4_{(\mathrm{O,N})}$ occurs.

As the cation ratios are the same for each glass and, as stated above, all Al is in four-fold coordination, the number of non-bridging electrons in the system is constant. Furthermore, it may be assumed that very few non-bridging nitrogens exist in these Er–Si–Al–O–N glasses. Based on these arguments, the decrease in Q^3 species and corresponding increase in Q^4 species can be visualised according to the schematic substitution given in Fig. 7(a). The alternative schematic substitution shown in Fig. 7(b) is less probable, as it will give rise to a local reorganisation of non-bridging oxygens (NBO) which may or may not be favourable, depending on the overall glass structure. Such a depiction of the change of Q^3 species to Q^4 species is consistent with other findings[33] where it was observed that more than 80% of nitrogen-containing tetrahedra in a Na–Si–O–N glass were present as SiO_3N tetrahedra, which is the case shown in Fig. 7(a). On the basis of the data and arguments given above, it can be concluded that the substitution of oxygen by nitrogen causes an increase in the crosslinking of the glass network via the transformation of Q^3 oxide species into Q^4 oxynitride species.

Clearly, it would be useful to compare the analyses presented here with those from another technique. However, in contrast to silicate glasses,[38,39] the addition of nitrogen causes



(a) oxide Q^3 species = oxynitride Q^4 species



(b) oxide Q^3 species oxynitride Q^4 species

Fig. 7. Possible structural changes generating (SiO_xN_y) Q^4 species (a) formation of Q^4 (SiO_3N with 1 NBO) from Q^3 (SiO_4 with 1 NBO), (b) formation of Q^4 (SiO_2N_2 with 2 NBO) from Q^3 (SiO_4 with 1 NBO).

MAS–NMR shifts to less negative ppm values, which is exactly the same effect observed in silicate glasses when Q^n n-values decrease. Other changes in peak positions observed previously in Y–Si–Al–O–N glasses using MAS–NMR[40] are not conclusive because of apparent phase separation effects. Therefore, it is thought that significant deconvolution routines for MAS–NMR data will need to be devised in order to fully quantify the fractions of each Q^n species. Lofaj et al.[25] attempted to do this for RE–Mg–Si–O–N glasses but the shifts ascribed to the SiO_3N tetrahedral unit do not correspond to MAS–NMR data of Kohn et al.[41] for Si–O–N glasses. Thus, it appears that the identification of Q^n species by the MAS–NMR technique requires a more detailed systematic analysis as in the study by Sen and Youngman[42] along with evidence from studies such as the present one using other techniques like Raman spectroscopy.

4. Conclusions

For Er–Si–Al–O–N glasses with cation ratio Er:Si:Al = 3.45:3:2 and nitrogen varying from 0 to 22 equiv.%, glass properties such as microhardness, glass transition temperature and dilatometric softening temperature all increased linearly with increasing nitrogen content.

Analysis of peaks from Raman spectra revealed that the best fit for the data for each of the glasses was a deconvolution for three peaks corresponding to Q^2–Q^4 structural units. It was shown that, as nitrogen content increases then the proportion of Q^3 species decreases and there is a corresponding increase in the proportion of Q^4 species, implying that a reaction of the type $Q^3_{\mathrm{O}} + \mathrm{N} = Q^4_{(\mathrm{O,N})}$ occurs, confirming that nitrogen increases the crosslinking between individual tetrahedra via the transformation of Q^3 oxide species into Q^4 oxynitride species.

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