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Compositional Effects on the Properties of Si-Al-RE-Based Oxynitride Glasses (RE = La, Nd, Gd, Y, or Lu)

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A series of silicon-aluminum oxynitride-glass compositions containing selected rare-earth (RE) additions were prepared to examine the effects of specific RE, as well as Si:Al:RE and N:O ratio, on properties. The properties that were characterized included density, thermal expansion coefficient (α), glass-transition temperature (T_g), hardness (H), and Young's modulus (E). The compositions (in equivalent percent) selected included: 55 Si-20 RE-25 Al oxide and 80 O-20 N oxynitride, and 45 Si-30 RE-25 Al oxide and 70 O-30 N glasses. The results show that the density increased significantly with an increase in the RE atomic mass and slightly with an increase in N:O ratio. For each of the fixed Si-Al-RE-O-N compositions, the E, H, and T_g values were each increased by substituting smaller RE ions, whereas the α value was decreased. For each specific cation composition and RE, increasing the N:O ratio systematically led to a decrease in the α values but an increase in the E, H, and T_g values. The observed response in the glass properties to changes in composition appears to reflect modifications in the bonding within the glass network.

I. Background

THE manner in which the composition of oxynitride glasses influences their properties is of considerable interest for at least two reasons. First, such glasses exhibit various properties that could be of interest for numerous applications. For example, the Si-Al-Y-O-N glasses (1) are very refractory, with a glass-transition temperature (T_g) >900°C, (2) have E values higher than those of oxide glasses, and (3) exhibit a range of α values.[1–5] Indeed, the properties apparently can be readily modified by tailoring the compositions. Studies[6–10] have shown that the substitution of lanthanide-series ions for yttrium can be used to modify elastic and thermal properties, as well as glass viscosity. Shelby and Kohli[11] observed an increase in α values and a decrease in T_g values as the rare-earth (RE) ion size increased in 50 Si-25 RE-25 Al oxide glasses. Ohashi *et al.*[9] found that both the E and T_g values increased with increases in the RE cationic field strength (valence/$(r^{3+})^2$, where r^{3+} is the radius of RE^{3+} in sixfold coordination) in oxynitride glasses with a composition of 64 Si-36 RE-20 N-80 O. In 56 Si-28 RE-16 Al-17 N-83 O glasses, Ramesh *et al.*[10] observed a decrease in α and an increase in H and T_g with an increase in cationic field strength of the RE. Increases in T_g with decreases in the RE ionic radius were found in both 51 Si-11 RE-38 Al-23 N-77 O and 40 Si-23 RE-37 Al-100 O glasses, and E increased with RE size in the latter glass.[7,8] In addition, the oxidation resistance of the Si-Al-RE-O-N glasses increased with decreases in the radius of the RE ion.[8] Finally, the refractive index (n) and magneto-optical properties of 50 Si-25 RE-25 Al oxide glasses were functions of the specific RE ion size (e.g., $n \propto 1/r^{3+}$) and content.[11,12]

Currently, considerable effort is underway to improve silicon devices by developing thin (<3 nm) film gate oxide films with increased dielectric constants. Silicon oxynitride materials are one class of materials being considered, where the dielectric constant (ε) has been observed to increase as n increases. In oxide glasses, ε can be increased by increasing n, through the substitution of RE ions of increasing size (e.g., ε increases from 3.81 for pure SiO_2 to 4.85 for Yb-SiO_2 to 4.95 for Ce-SiO_2).[13] Similar effects resulting from RE substitutions should be expected in the oxynitride glasses.

A second reason for the interest in oxynitride glasses is that amorphous silicon-based oxynitride intergranular phases form in Si_3N_4 ceramics when densification additives (e.g., RE_2O_3, Al_2O_3) react with the native oxide species in the Si_3N_4 powders. The resultant amorphous intergranular phases affect the mechanical behavior, at both room temperature and elevated temperature, of the Si_3N_4 ceramics. For instance, residual stresses are introduced because of the mismatch in thermal expansion and elastic properties between the glass and crystalline phases. The residual stresses can introduce local cracks and alter the strength of the ceramic. An intergranular glass whose viscosity decreases rapidly with increases in temperature can limit the creep resistance of the polycrystalline ceramics. However, the formation of a glassy phase is very beneficial, because it promotes sintering by liquid-phase densification and serves as a medium for grain growth. It would be desirable to generate limited amounts of glass phase with higher T_g values to improve the creep response and yet retain the attributes of liquid-phase sintering. Thus, one needs to know how to tailor the properties of the intergranular glasses to also improve the performance of the Si_3N_4 ceramics.

The present study sought to evaluate the properties of four glass compositions: 55 Si-20 RE-25 Al with both 0 N-100 O and 20 N-80 O, and 45 Si-30 RE-25 Al with both 0 N-100 O and 30 N-70 O (in equivalent percent (eq.%)). These compositions were based on earlier phase equilibrium studies conducted on various Si-Al-RE-O-N systems.[14,15] The rare earths included La, Nd, Gd, Y, and Lu, which, with the possible exception of Nd, only exhibit a valence of 3+. This choice was made to eliminate any ambiguities that might result from concerns with the actual valence of the RE ions in the glass (e.g., Ref. 10). To expand our knowledge of the composition–property relationships, the density, thermal expansion coefficient, glass transition temperature, hardness, and Young's modulus for each of these glass compositions were evaluated.

II. Experimental Procedure

Powder precursors were formulated by mixing the proper amounts of Si_3N_4 (E-10, UBE Industries, Ltd., Yamaguchi, Japan), Al_2O_3 (AKP-50, Sumitomo Chemical Co., Ltd., Tokyo, Japan), and Re_2O_3 (Gd_2O_3, Nd_2O_3, and Lu_2O_3 from Stanford Materials, San Mateo, CA; Y_2O_3 and La_2O_3 from Molycorp, Fairfield, NJ) powders. Samples were prepared from powder mixtures of the following compositions (in eq.%): 55 Si-20 RE-25 Al-100 O, 55 Si-20 RE-25 Al-20 N-80 O, 45 Si-30 RE-25 Al-100 O, and 45

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Si-30 RE-25 Al-30 N-70 O. The samples were cold-pressed at ~7 MPa to form ~5 g pellets ~1.25 cm in diameter and ~1 cm high. The cold-pressed pellets were then placed inside a covered BN-coated graphite or BN crucible. In the case of the oxynitride glasses, this crucible was then placed on a BN powder bed inside a larger graphite crucible (see Fig. 1). Next, the oxide or oxynitride glass plus container were placed in a gas-pressure-sintering furnace (Model 612 high-pressure furnace, Thermal Technologies, Inc., Concord, NH) and heated to 1000°C under vacuum (~0.1 torr (1 torr = 1.3332×10^2 Pa)). For the oxynitride glasses, nitrogen was introduced at 1000°C to a pressure of 5 MPa, and those conditions were maintained for the rest of the heating and cooling cycle. For the oxide glasses, an argon gas overpressure of 5 MPa was introduced at 1000°C, and the conditions were maintained through the rest of the heating and cooling cycle. In a limited number of trial oxide-glass melts, a vacuum was maintained throughout the run; there was no clear benefit from this modification. The heating schedule was as follows: The temperature was increased to 1000°C in 2 h, followed by a 10 min hold. After this hold, the temperature was increased to the desired melting temperature (1650°–1750°C) in 1 h and held there for ~20–30 min. The cooling portion of the schedule consisted of shutting the power off, which resulted in a measured cooling rate of ~35°C/min from the melting temperature to 1000°C, after which the rate decreased to ~15°C/min. The gas-pressure furnace system eliminated the opportunity to quench the samples, as done in other studies.

After the samples had been cleaned, they were sectioned and examined optically, to determine whether bubbles or inclusions were present. X-ray diffraction analysis was also conducted to detect the presence of any crystalline phases, and only materials free of crystalline phases and bubbles were used for further measurements. The densities of the glasses were determined in distilled water at 22°C, using Archimedes' principle. Sections of each glass were used for further characterization: One piece was mounted and polished for indentation studies and analytical microscopy, one section was used to characterize oxygen and nitrogen content, and another section was machined to form a bar for thermal expansion analysis. The final nitrogen and oxygen contents of the glasses were determined by hot-gas-extraction analysis (LECO Corp., St. Joseph, MI); the cation contents had been confirmed using analytical software (DSTA, National Institute of Standards and Technology (NIST), Gaithersburg, MD) to analyze energy-dispersive data obtained by spectrometry mounted on a field-emission-gun scanning electron microscope. The glass characteristics and compositions are shown in Table I.

The H values of the glasses and their E values were obtained using an instrumented nanoindenter system (Nanoindenter II, MTS/Nano Instruments, Oak Ridge, TN) equipped with a Berkovich indenter and the data analyzed per the procedures of Oliver and Pharr.[16] Linear α values were calculated over the range 22°–622°C, from data obtained using a dual-rod dilatometer (1600°C dilatometer, Theta Industries, Port Washington, NY), with the sample deflection compared with that of a NIST sapphire standard. Before the start of each dilatometer run, the sample chamber was evacuated and then back-filled with nitrogen, with the test conducted in flowing nitrogen. The runs were conducted over the range 22°–700°C, at heating/cooling rates of 1°C/min. T_g values were determined by heating to 600°C at 2°C/min, then heating to a maximum temperature (<1100°C) at a rate of 1°C/min, with the transition point defined as the inflection point associated with the onset of permanent deformation of the glass sample.

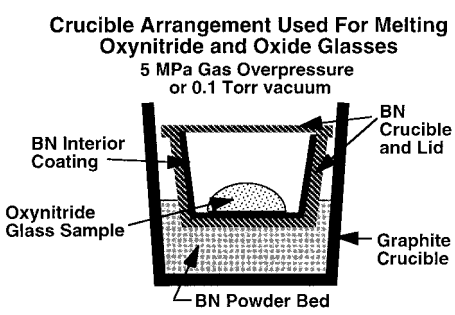

Fig. 1. Configuration of experimental glass-melting crucible used to form oxynitride glasses.

III. Results

The following section describes the observed trends in glass properties, including the effects of composition on the density and α, T_g, and E values with composition. The compositional variations were selected to allow assessment of the effects of the N:O and the Si:Al:RE ratios, as well as of the ionic radii of the rare earths (e.g., La, Nd, Gd, Y, and Lu). When the RE was Lu, the nitrogen content in the oxynitride glasses was 70%–80% of the formulated compositions; all other RE oxynitride glasses had nitrogen contents essentially equal to those of the formulated compositions.

The density of glass samples for each composition increased when RE ions of greater atomic mass (Table II) were substituted into the glasses, as shown in Fig. 2. Similar effects were observed by Kohli and Shelby[6] (Fig. 2), as well as by Ohashi *et al.*[9] and Ramesh *et al.*[10] In the present case, this effect was enhanced when the Si:RE ratio was decreased (e.g., compositions of 55 Si-20 RE-25 Al versus 45 Si-30 RE-25 Al). In addition, a slight increase in density with an increase in nitrogen content in the glass network was observed; however, this particular effect appears to have diminished when the Si:RE ratio increased.

The linear α values were quite sensitive to composition, as shown in Fig. 3. For each cation composition (e.g., 45 Si-30 RE-25 Al and 55 Si-20 RE-25 Al), the coefficients decreased systematically as the RE ionic radius decreased, which also increased the cationic field strength in both oxide and oxynitride glasses. Ramesh *et al.*[10] and Shelby and Kohli[11] observed similar trends for decreasing expansion coefficients as the RE ionic radius decreased (the RE field strength increased). Our findings show that α also decreased for each cation composition when either the N:O or the Si:RE ratio increased.

The T_g values of all of the glasses examined here increased substantially with an increase in the nitrogen content (Figs. 4 and 5), a trend also noted by Tanabe *et al.*[7] As noted in earlier observations,[6–10] decreasing the RE ion size increased the T_g values. Although the dependence of T_g on the RE cationic field strength is clearly shown in Fig. 5, the potential effects of changes in the Si:RE ratio (e.g., in 45 Si-30 RE-25 Al versus 55 Si-20 RE-25 Al) are not well-defined. The T_g-versus-RE field strength trend found for the current 45 Si-30 RE-25 Al oxide glasses was comparable to those observed earlier for the 50 Si-25 RE-25 Al oxide glasses.[11]

For each of the four compositions, the E values systematically increased with the incorporation of RE ions of decreasing ionic size (Fig. 6), a result similar to that noted in earlier work.[7,9] In addition, in the present study, the E values increased as the N:O ratio of the 45 Si-30 RE-25 Al and the 55-Si-20 RE-25 Al glasses increased; a similar trend was noted in Si-Al-Y glasses.[5] In both the oxide and the oxynitride glasses, replacing a portion of the Si ions by RE ions also increased the E values.

The H values of the present glass compositions increased with increases in the cationic field strength of the RE present (Fig. 7). At the same time, H increased substantially with an increase in the nitrogen content of the glasses. Finally, both the oxide and the oxynitride glasses exhibited an increase in H when the Si:RE ratio of the glass was increased.

IV. Discussion

(1) Bulk Density

The increase in the density for each composition accompanying the substitution of various RE elements simply reflects the increase

Table I. Oxide and Oxynitride Glasses

As-formulated compositions	As-melted glasses: Characteristics†	As-melted glasses: Composition (equiv.%)
Oxide-glass composition (equiv.%)		
55 Si-20 La-25 Al-100 O	Gray, translucent	100 O‡
45 Si-30 La-25 Al-100 O	Gray tint, translucent	100 O‡
55 Si-20 Nd-25 Al-100 O	Red, translucent	100 O‡
55 Si-20 Gd-25 Al-100 O	Dark gray, translucent	100 O‡
45 Si-30 Gd-25 Al-100 O	Translucent	100 O‡
55 Si-20 Lu-25 Al-100 O	White tint, translucent	100 O‡
45 Si-30 Lu-25 Al-100 O	Translucent	100 O‡
Oxynitride-glass composition (equiv.%)		
55 Si-20 La-25 Al-80 O-20 N	Gray, translucent	53 Si-19 La-28 Al-79 O-21 N
45 Si-30 La-25 Al-70 O-30 N	Translucent	46 Si-28 La-26 Al-71 O-29 N
55 Si-20 Nd-25 Al-80 O-20 N	Red, translucent	82 O-18 N‡
45 Si-30 Nd-25 Al-70 O-30 N	Gray, translucent	49 Si-24 Nd-24 Al-72 O-28 N
55 Si-20 Gd-25 Al-80 O-20 N	Gray tint, translucent	57 Si-19 Gd-24 Al-81 O-19 N
45 Si-30 Gd-25 Al-70 O-30 N	Gray tint, translucent	48 Si-30 Gd-22 Al-69 O-31 N
55 Si-20 Lu-25 Al-80 O-20 N	Gray tint, translucent	59 Si-18 Lu-23 Al-84 O-16 N
45 Si-30 Lu-25 Al-70 O-30 N	Gray tint, translucent	49 Si-29 Lu-22 Al-79 O-21 N
45 Si-30 Y-25 Al-70 O-30 N	Gray	47 Si-30 Y-23 Al-69 O-31 N

†X-ray diffraction results confirmed the amorphous nature of the glasses. ‡Cation content not determined.

in the atomic mass of the RE elements themselves (Fig. 2, Table II). This effect was further enhanced when more of the lower-atomic-mass cations (e.g., the Si) were replaced by the RE ions. The small increase in densities associated with an increase in the N:O ratio is attributed to an increase in atomic packing of the network, resulting from the threefold coordination of nitrogen with silicon versus the twofold coordination of oxygen with silicon.[3] The lower nitrogen contents of the lutetium-based oxynitride glasses had no discernible affect on this trend. These increases in oxynitride-glass density with RE substitution (e.g., 3.5–5.5 g/cm^3) are of interest to those characterizing Si_3N_4 (~3.2 g/cm^3) ceramics, because incorporating intergranular amorphous phases modifies the theoretical density of the ceramic.

(2) Thermal Expansion Coefficients and Glass Transition Temperatures

The thermal expansion coefficients for each cation composition (45 Si-30 RE-25-Al and 55 Si-20 RE-25 Al) clearly increased as the size of the RE ion increased and as the nitrogen content decreased (Fig. 3). The expansion coefficients are associated with the asymmetry in the interatomic potentials and, thus, the atomic thermal vibrations. The primary vibration modes in glasses include either nonbridging oxygens (NBOs) or nonbridging nitrogens (NBNs) with network formers (e.g., Si, Al), because they modify the expansion coefficients, and bridging oxygens (BOs) or bridging nitrogens (BNs) with network formers, because they strengthen the network.[3,18] Studies of Si-Al-Y-O-N glasses indicate that the increased expansion coefficients with yttrium substitution for aluminum are associated with an increase in the number of NBOs.[3] Increases in NBO contents with an increase in RE content have also been observed,[18] which would explain the increases in coefficients with an increase in the Si:RE ratio of the current glasses noted here.

In crystalline oxides, the coordination of RE solutes can also increase as the size of the RE ion increases;[19] similar effects have been indicated for glasses that contain RE additions.[20] An increase in coordination of the RE ion with oxygen ions could increase the fraction of NBOs, a result similar to that created with increases in RE content. This change would be consistent with the observed increase in α values, for each glass composition, with increases in the size of the RE ion. On the other hand, it had been concluded earlier that the glass structure (fraction of NBO versus BO) was not a significant factor in the expansion of one Si-Al-RE-O-N glass composition that contained various RE ions.[10] In that study, the decrease in expansion coefficients was associated with an increase in the field strength of the smaller RE ions (Table II). It was felt that stronger RE—O (RE—N) cross-linking bonds between network chains would result. At this point, one can only suggest that variations in both the cross-linking RE bonds and the NBO content with RE ion size may be factors.

The substitution of nitrogen for oxygen within the current glasses resulted in a significant decrease in α values. The lower nitrogen content of the 45 Si-30 Lu-25 Al-21 N glass may be reflected in a somewhat higher than expected α value, as compared with the trend for the other RE glasses of this group. Rouxel *et al.*[21] indicated that the short-range order of Si-Al-Y-O-N glasses can increase as the nitrogen content increases, likely related to the higher coordination of nitrogen with cations, as compared with that for oxygen. This increase should result in more cross-linking between structural tetrahedra and strengthen the network. In the analysis of Si-Al-Y-O and Si-Al-Y-O-N glasses by Jin *et al.*,[20] nitrogen appeared to substitute for both bridging and nonbridging

Table II. Characteristics of Cations in Glasses

Characteristic	Value: Si	Al	Lu	Yb	Y	Gd	Nd	La
Ionic radius† (Å)[17]	0.39	0.75	0.85	0.87	0.90	0.94	0.98	1.05
Typical valence	4+	3+	3+	3+	3+	3+	3+	3+
Outer-shell electrons	Ne	Ne	Xe $4f^{14}$	Xe $4f^{13}$	Kr	Xe $4f^{7}$	Xe $4f^{3}$	Xe
Other valences				2+			2+ 4+	
Atomic weight (g)	28.09	26.98	174.97	173.04	88.91	157.3	144.2	138.9

†Ionic radii for RE and Y given for coordination number of 6.

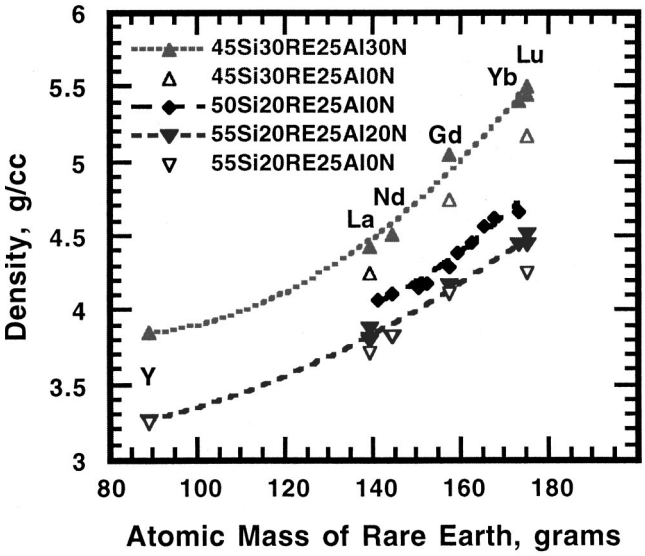

Fig. 2. Plots showing that the densities for each glass composition vary systematically with the atomic mass of the RE. Replacing the Si ions with RE ions substantially increases the density, whereas increasing the nitrogen content has a smaller effect. Compositions are given in equivalent percent; data for 50 Si-25 RE-25 Al oxynitride glasses from Kohli and Shelby.[6]

oxygens. Based on nearest-neighbor coordinations of RE ions, others have suggested that a small fraction of nonbridging nitrogens are also present in Si-Al-RE-O-N glasses.[22] However, observations of nitrogen-to-silicon coordination of ~2.9 versus 3.0 indicate that most of the nitrogen forms bridging bonds.[20] It is concluded that the main role of the substitution of nitrogen for oxygen must lie in decreasing the number of nonbridging anion bonds.

As noted by Buri *et al.*,[23] the T_g value is a function of atomic packing of the network and the strength of the cation–anion bonds. Increases in cation and anion coordination would effect an increase in packing density. Thus, an increase in T_g would be expected as the nitrogen content of the glasses increased (Fig. 4), because of an increase in coordination of the anion and the stronger covalent Si—N versus Si—O bond. The data for the Si-Al-Lu-O-N glasses,

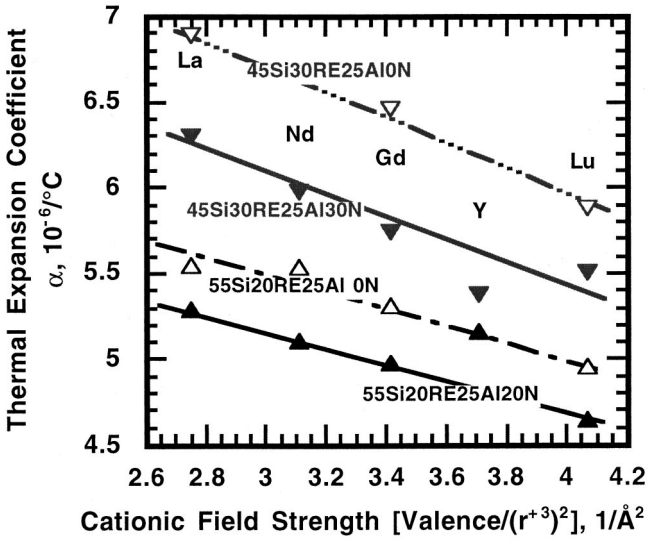

Fig. 3. Plots showing that the linear α value (22°–622°C) for each specific glass composition decreases with increased field strength (i.e., with decreasing ionic radius, r^{3+}; see Ref. 17) of the lanthanide ion. Decrease of either the nitrogen or the silicon content increases the value of the expansion coefficients.

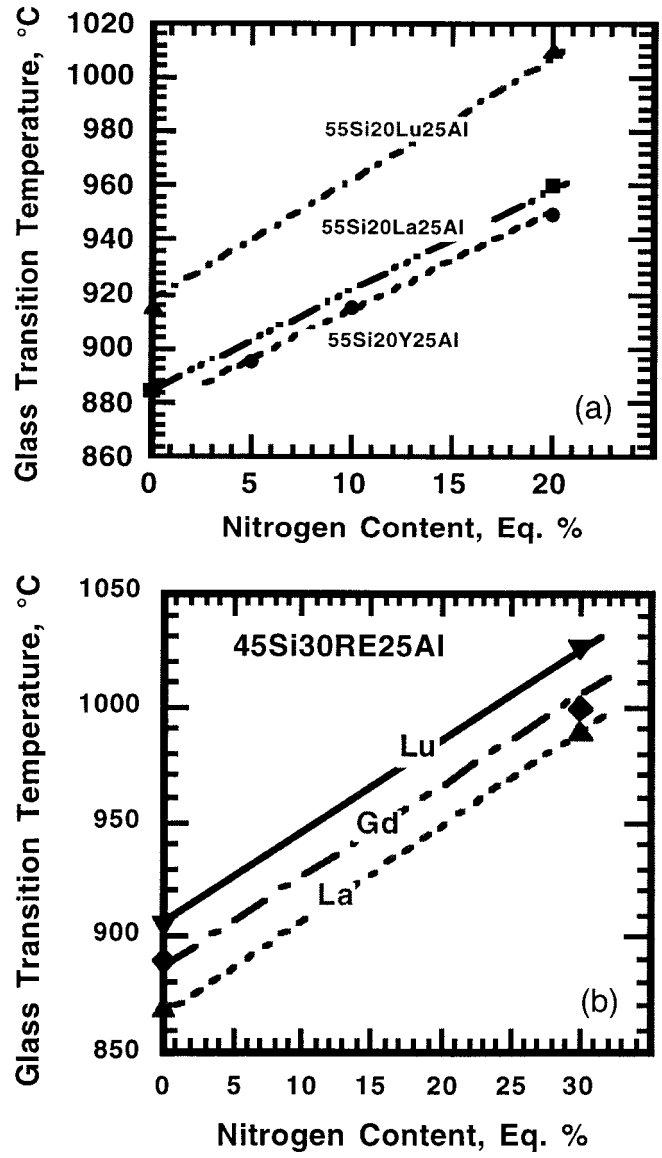

Fig. 4. Plots showing that increasing the N:O ratio of the (a) 55 Si-20 RE-25 Al and (b) 45 Si-30 RE-25 Al oxynitride glasses increases T_g, which shifts the viscosity–temperature curve to a higher-temperature region. In addition, higher T_g values are obtained with the use of lanthanide ions with smaller ionic radii and larger field strengths. Data for 55 Si-20 Y-25 Al glasses were taken from Sun *et al.*[5]

with their somewhat lower nitrogen contents, do not appear to alter this trend significantly. The increase in T_g with a decrease in the ionic radius of the RE (Fig. 4) is consistent with the accompanying increase in bond strengths, as reflected in increased cationic field strengths (Fig. 5). Thus, as in the case for the α values, the effect of the RE ions appears to correlate with the changes in the bonding between the RE and the anions.

(3) Young's Modulus and Microhardness

Young's modulus and microhardness are primarily a function of the bond strength within the glass network, as well as the strength of cross-linking bonds. Molecular orbital calculations show that the presence of a corner-sharing nitrogen (as opposed to oxygen) between two $Si(N,O)_4$ tetrahedra increases the resistance to bending and stiffens the network.[24] Thus, not surprisingly, both E and H increase as nitrogen replaces oxygen in the glass network, even as the Si:RE ratio increases, in the current glasses. The somewhat lower nitrogen contents of the Si-Al-Lu-O-N glasses appears to have a greater effect on the

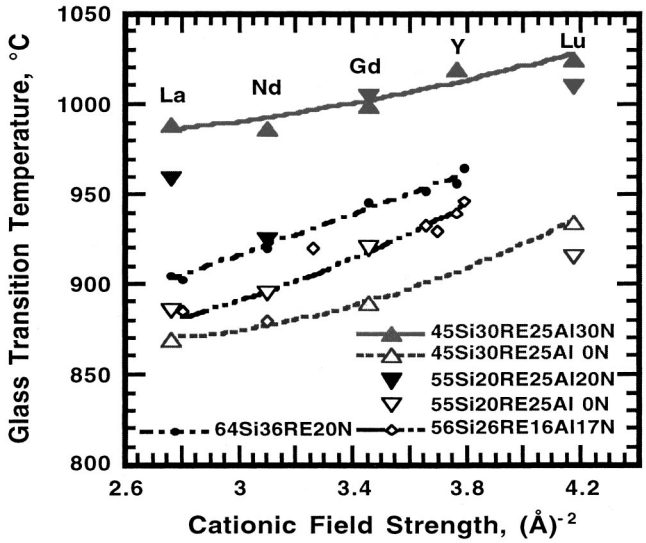

Fig. 5. Graph showing that the increase in T_g can also be correlated with an increase in the cationic field strength of the RE ions, for both the oxide and oxynitride glasses. Data for glass composition (●) 64 Si-36 RE-20 N (from Ohashi *et al.*[9]) and (◇) 56 Si-26 RE-16 Al-17 N (from Ramesh *et al.*[10]) are included for comparison.

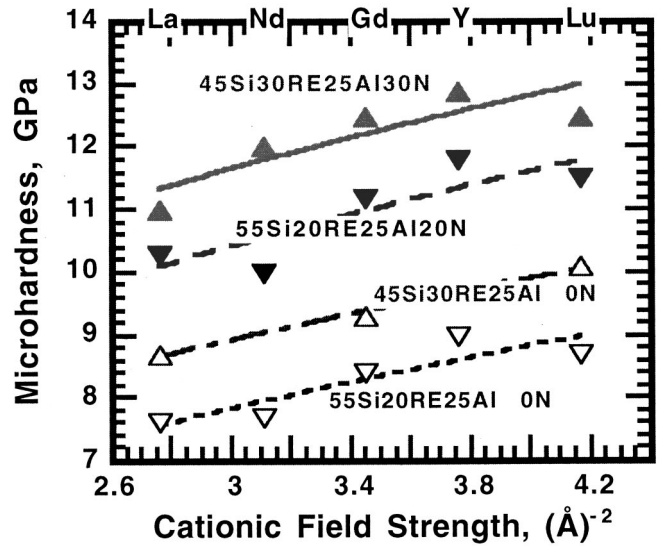

Fig. 7. Graph showing that the microhardness values of the Si-Al-RE-O and Si-Al-RE-O-N glasses increase as a function of the cationic field strength of the RE ion and the nitrogen content of the glass.

trends in E and H, which is consistent with a loss of stiffness of the network. The trend for increasing E and H values with the incorporation of the smaller rare earths is consistent with a strengthening in the network bonds resulting from the increases in the field strength of the RE—O bond. In addition, X-ray studies of Si-Al-RE-O-N glasses where the RE is either La, Gd, or Yb indicate that both RE—O and RE—N bonds can be present.[22] The presence of RE—O and RE—N bonding could further enhance the strength of the network by forming cross-links between chains of network tetrahedra. The observed increases in E and H with increases in the Si:RE ratio for the oxide glasses are somewhat surprising. This finding suggests that RE ions form strong cross-linking bonds (e.g., Si—O—RE—O—Si or Si—O—RE—O—Al) between silicon or aluminum body-centered-tetrahedra network chains to strengthen the glass network. In the case of the oxynitride glasses, the increase in Si:RE ratio is accompanied by an increase in N:O ratio, and the N:O ratio is a major factor in the increase of E and H. However, the results in the oxide glasses imply that the rare earths also contribute significantly to the glass network strength.

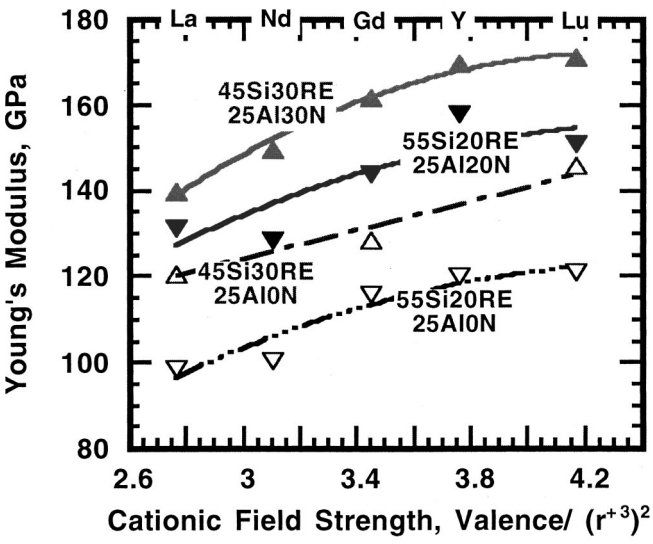

Fig. 6. For each specific glass composition, the Young's modulus increases with cationic field strength (or with decrease in the ionic radius of the RE ion). Incorporating nitrogen into the glass increases the moduli more significantly, particularly for the glass with the higher silicon content.

V. Conclusions

The properties of the Si-Al-RE-O-N glasses (RE = La, Nd, Gd, Y, and Lu) can be readily tailored by controlling both the N:O and Si:RE ratios, as well as by the specific RE ion incorporated into the glass. For instance, the bulk density increases substantially with both the atomic mass and the amount of the RE ion and exhibits a small increase as the N:O ratio increases. With a decrease in RE ion size, the T_g, E, and H values increase, whereas the α value decreases, in each composition. In each case, the properties for a given composition correlate with the change in cationic field strength of the RE, indicative of a strengthening of the glass network. However, the response of the expansion coefficients must also reflect a change in the number of nonbridging anions. This change is seen in the increased α values with increased Si:RE ratios in both the oxide and oxynitride glasses. Interestingly, both the E and H values of the oxide glasses increase as the Si:RE ratio increases. This result suggests that the RE ions can generate strong cross-linking bonds, which more than compensate for the loss of Si—O bonding. Finally, increases in the N:O ratios of these glasses substantially increase the E, H, and T_g values and decrease the α values, results that are indicative of changes in network strength and nonbridging anion contents.

Acknowledgments

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