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Thermal expansion and glass transition temperature of the rare-earth doped oxynitride glasses

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Abstract

Thermal expansion coefficients (α), glass-transition (T_g) and Littleton (T_L) temperatures, hardness and density of the RE–Si–Mg–O–N glasses (RE = Sc, Y, La, Nd, Sm, Gd, Yb, and Lu) were investigated to separate the effects of rare-earth elements and nitrogen on the properties of bulk glasses. These properties depend approximately linearly on nitrogen content, density of the glass and ionic radius of the corresponding lanthanide. Lanthanides modify hardness of the studied oxynitride glasses with 20–24 eq.% N by 11.4–14.4%, α by ~13%, T_g by 31–35 °C, and T_L by 33–43 °C. Deviations from linearity found in Nd-, Sm- and Yb-doped glasses were possibly due to valence change. Non-lanthanide dopants, Sc and Y, often do not fit the dependence but result in comparable properties. The effects of nitrogen and rare-earth dopants are independent and additive.

Keywords: Glass; Glass transition temperature; Hardness; Oxynitride glass; Thermal expansion

1. Introduction

The development of nano-ceramics is one of the very promising ways to reach properties and effects, which are not possible in the "conventional" structural ceramics with typical grain size of around one micron. However, silicon nitride based materials contain amorphous phases at the grain boundaries as a consequence of densification process. This residual glass is present as approximately 1 nm thin intergranular film (IGF) at two-grain interfaces. They consist of the oxynitride glasses with various rare-earth elements[1] originating from sintering additives. The reduction of the grain size of the primary phase in nano-ceramics would result in significant increase of the surface to volume ratio of the primary phase and substantial increase of the IGF area, while the thickness of these films remains approximately the same. Thus, the role of the residual glassy phase as a factor controlling properties of these materials, especially at elevated temperatures, will dramatically increase.

Direct investigation of the properties of the intergranular films is experimentally very difficult not only due to their small size but also because they exist only as a part of polycrystalline ceramics. Even properties of the bulk oxynitride glasses with the composition similar to that of IGF are not well known. Such oxynitride glasses are of interest for the development of advanced ceramics but also because their properties are usually better than those of oxide glasses. Moreover, their structure and final properties can be modified by tailoring the composition using two different approaches.[2–10] Nitrogen, which acts as a network former, is directly bonded to silicon in the glass.[2–7,11,12] Because of higher valence of nitrogen, partial substitution of oxygen by nitrogen in the network produces tighter and more linked structure. It results in linear increase in density,[4,10,13–17] hardness,[3,4,8,9,15,17] Young's modulus,[8,13,16–18] thermal expansion coefficient,[4,6,9,13,19,20] glass transition temperature,[4,6,9,13,19,20] viscosity[9,14,15,21] etc. For instance, adding 20 eq.% of N resulted in 33% increase in La- and 23% increase of elastic modulus in Lu-containing oxynitride glasses.[17] The presence of 4.8% of N in Y–SiAlON glass increased its viscosity at elevated temperatures by three orders of magnitude in comparison with the corresponding oxide glass.[21]

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Tailoring the properties via rare-earth additives involves the effects of coordination numbers and bond strength between elements in the glass. Cations with higher coordination numbers strengthen glass structure and increase glass transition temperature.[7] When various cations with the same coordination number are used, glass structure and properties depend on the field strength of the cation. Lanthanide cations are often used because of so called ''lanthanide contraction''. All lanthanides have very similar electron structure, [Xe] $4f^x$ $5d^0$ $6s^2$, with x increasing from 2 for Ce up to $x=14$ for Yb. Shell d is occupied by one electron only in the case of La, Gd and Lu. In contrary to general expectations, atomic and ionic radii of lanthanides regularly decrease with the increase of the atomic number and f-shell occupancy. Lanthanides are assumed to act in the glasses as network modifiers, which are incorporated in the space between Si-$(O,N)_x$ tetrahedra. The network with smaller atoms, e.g. with Yb or Lu, would have tighter structure and better properties than the glasses containing lanthanides with greater ionic radii. For example, the replacement of La by Lu in oxide glasses caused 21–25.5% and 16–22% increases in the Young's modulus in oxide and oxynitride glasses, respectively; hardness increased by 13–16%.[17] Glass transition temperatures in La-glasses without and with 20 eq.% of N were approximately 882 and 960 °C, whereas they were ~916 and ~1010 °C in Lu-containing glasses.[17] The other studies on glasses with different rare earth-containing additives reported comparable changes.[8,9,12,13,15,16,18–20]

The property changes follow usually linear dependence on ionic radii or cationic field strength (CFS) of the corresponding rare-earth elements. CFS is defined as

$$\mathrm{CFS} = Z/r^2,$$

where Z is the valence of the corresponding element in the oxide compounds and r is its ionic radius. Ionic radii reported by Shannon[22] were used in the calculation of CFS. The deviations from linearity are observed in non-lanthanide additives but also in some lanthanides.[15,16,23–26] In the case of Eu, different valence and higher coordination number in lanthanides with high atomic numbers were considered as the reasons for variation in property dependencies.[16] Our previous studies on RE-Si–Mg–O–N glasses (RE = Sc, Y, La, Sm, Yb and Lu) confirmed the deviations from linear dependence of microhardness and indentation moduli at room temperature in the case of Sc- and Y-containing oxynitride glasses.[23,24] At elevated temperatures, glass transition temperature (T_g) of Y-containing glass fit the dependence while T_g of Yb-containing glass was off.[25] Despite unsupported assumptions about possible changes in coordination numbers, the nature of these deviations was unclear. Moreover, the analysis was hampered by possible influence of inhomogeneities and insufficient number of lanthanide dopants in the studied glasses. Material preparation procedure in the current study has been therefore modified to improve the homogeneity of the glasses, glasses with additional two rare-earth additives and wider nitrogen content range were produced and another experimental techniques were used. The RE/Mg ratio was kept intentionally constant and only O/N ratio varied to separate effects of nitrogen and RE without influence of Mg. The aim of this work is to investigate separately the effect of nitrogen, lanthanide and non-lanthanide additives on selected properties of the oxynitride glasses at room and elevated temperatures to understand possibilities for tailoring glass properties and underlying glass structure changes.

2. Experimental procedure

2.1. Glass preparation

Twenty glass formulations have been prepared from the mixtures of powders of SiO_2 (Aerosil OX 50, Degussa-Hüls AG, Germany) + MgO (MgO 500 A, UBE Ind. Ltd., Japan) + α-Si_3N_4 (SN-E10, UBE Ind. Ltd., Japan) + RE_2O_3 (RE = Sc (Scandium Oxide, Meldform Rare Earths Ltd., UK), Y (Yttriumoxid feinst, H. C. Starck, Germany), La (Lanthan (III)-Oxid, Merck, Germany), Nd, (Neodymium (III) oxide 99.9%, Alfa Aesar, Johnson Matthey GmbH, Germany), Sm (Samarium Oxide, Meldform Rare Earths Ltd., UK), Gd (Gadoliniumoxid 99.9%, Treibacher Auermet GmbH, Austria), Yb (Yb_2O_3 99.99%, Shin-Etsu Chem. Co., Ltd., Japan) or Lu (Lutetium oxid 99.9%, Treibacher Auermet GmbH, Austria) as described earlier.[26] The choice of rare-earth dopants was directed by an attempt to map consistently the effects of the elements from lanthanide group (La, Nd, Sm, Gd, Yb and Lu) and from third group in the periodic table (Sc, Y and La), which are often treated the same way as lanthanides. The valence of all these elements is typically +3, however, Nd, Sm and Yb can also occur in +2 valence. The ratio Mg: RE of 1:1 was constant and 20 eq.% for each element. The amount of silicon nitride powder in the formulations was calculated in such a way that the resulting nitrogen contents were 20 eq.% or 24 eq.%. In the case of La, additional glasses containing 0, 10, 22 and 28 eq.% of nitrogen were prepared to investigate its pure effect without influence of other rare-earth dopants. The compositions of the individual powder mixtures in equivalent%, molar% and weight% are summarized in Table 1. The abbreviation of glasses in Table 1 consists of RE element and N with its content in eq.%.

The powder formulations (25 g per batch) were homogenized in a planetary mill with 2-propanol and silicon nitride balls. The batches were subsequently

Table 1
The composition of the powder mixtures used for the preparation of the glasses

Glass system	Eq.%					Mol.%				Wt.%			
	Si	RE	Mg	O	N	RE_2O_3	SiO_2	MgO	Si_3N_4	RE_2O_3	SiO_2	MgO	Si_3N_4
ScN20	60	20	20	80	20	13.4	39.7	40.1	6.8	27.1	35.4	23.7	13.8
ScN24	60	20	20	76	24	13.7	36.6.	41.2	8.4	27.3	32.1	23.9	16.7
YN20	60	20	20	80	20	13.4	39.7	40.1	6.8	37.8	30.2	20.2	11.7
YN24	60	20	20	76	24	13.7	36.6	41.2	8.4	38.1	27.4	20.4	14.5
LaN0	60	20	20	100	0	11.8	52.9	35.3	0	45.4	37.7	16.9	0
LaN10	60	20	20	90	10	12.5	46.7	37.5	3.2	46.1	31.9	17.1	5.0
LaN20	60	20	20	80	20	13.4	39.7	40.1	6.8	46.7	25.9	17.3	10.1
LaN22	60	20	20	78	22	13.5	38.2	40.6	7.6	46.9	24.6	17.4	11.1
LaN24	60	20	20	76	24	13.7	36.6	41.2	8.4	47.0	23.4	17.4	12.1
LaN28	60	20	20	72	28	14.1	33.3	42.4	10.1	47.3	20.9	17.5	14.2
NdN20	60	20	20	80	20	13.4	39.7	40.1	6.8	47.5	25.5	17.1	9.9
NdN24	60	20	20	76	24	13.7	36.6	41.2	8.4	47.8	23.1	17.2	12.0
SmN20	60	20	20	80	20	13.4	39.7	40.1	6.8	48.4	25.0	16.8	9.7
SmN24	60	20	20	76	24	13.7	36.6	41.2	8.4	48.7	22.7	16.9	11.8
GdN20	60	20	20	80	20	13.4	39.7	40.1	6.8	49.4	24.6	16.5	9.6
GdN24	60	20	20	76	24	13.7	36.6	41.2	8.4	49.7	22.2	16.6	11.5
YbN20	60	20	20	80	20	13.4	39.7	40.1	6.8	51.5	23.6	15.8	9.2
YbN24	60	20	20	76	24	13.7	36.6	41.2	8.4	51.8	21.3	15.9	11.1
LuN20	60	20	20	80	20	13.4	39.7	40.1	6.8	51.7	23.4	15.7	9.1
LuN24	60	20	20	76	24	13.7	36.6	41.2	8.4	52.0	21.2	15.8	11.0

The designation of the samples indicates type of rare-earth element and nitrogen content in eq.%.

dried at 60 °C and sieved. Cylinders of 23 mm in diameter and 10–13 mm in height were obtained from ~10 g of powder mixtures after uniaxial and cold isostatic pressing under pressures of 20 and 400 MPa, respectively. The green body was sintered in a powder bed of an equimolar mixture of the corresponding glass formulation and boron nitride in a boron nitride crucible. The crucible was placed in larger graphite crucible with a powder bed of SiO_2 and Si_3N_4 in a graphite-heated gas pressure sintering furnace (KCE Sondermaschinen GmbH, Germany). The samples were heated up to 1700 °C and held under 2 MPa of nitrogen pressure for 0.5 h. The furnace heating was then switched off and the melts cooled with the rate app. 25 K/min above 1100 °C. The obtained samples were rounded pellets with a flat bottom and slightly rounded top surface. Their weight loss during sintering of only 2–5% suggests that the composition of the bulk glasses is close to that in the powder batches. The determination of the true nitrogen and oxygen contents in the obtained glasses is a subject of a future work. Specimens with the size of approximately 3 mm×4 mm×10.5 mm and 1.3 mm thin cross sections were then cut and polished for dilatometry, hardness, optical microscopy and other experiments.

2.2. Microstructure and density studies

The visual observations and optical microscopy at 500×magnification were performed on the polished surfaces of each glass to investigate homogeneity of glasses and to determine the extent of partial glass crystallization. X-ray diffraction studies were performed on conventional X-ray diffraction apparatus (D500 Kristalloflex, Siemens, Germany) in order to reveal the degree of devitrification and to identify possible crystalline phases. Density measurements were performed on the polished samples for thermal expansion coefficient measurements using Archimedes method in distilled water at 22 °C.

2.3. Microhardness

The microhardness for each of the glass systems studied was measured using semi-automatic microhardness tester (Model AVK-C1, Akashi, Japan) with a load of 500 g using a Vickers indenter. Indentation was automatic with a pre-determined dwell time of 10 s. The size of both diagonals was measured semi-automatically. The absolute hardness values were calculated automatically according to the well known formula and expressed in conventional units HV,

$$\mathrm{HV} = 0.1854\ P/d^2,$$

where d is the average of two indentation diagonals in mm and P is the loading force in N. At least 10 indents were used to get the mean value of microhardness and corresponding standard deviation.

2.4. Dilatometry

Two series of dilatometric experiments were performed in a horizontal dual-rod dilatometer (Model DIL 602,

Bähr Thermoanalyse GmbH, Germany) in flowing N_2, and heating rate of 1 K/min and sapphire standard. The first set of experiments on as-produced samples was used to estimate T_g. Each glass was then annealed for 1 h in air at temperature approximately 10 °C above such fictive temperature and then slowly cooled to reduce the prehistory effect. Second set of dilatometric experiments on the pre-annealed samples yield final data. Automatic switch off function was used to prevent excessive deformation of the sample at temperatures above dilatometric softening point. Thermal expansion coefficients, α, were determined from the experimental curves for temperature difference between room temperature (22 °C) and 522 and 722 °C. T_g was determined as the intersection of the linear extrapolation of the slope of thermal expansion curve of the solid glass and that of the glass "melt". Littleton temperature, T_L, sometimes also called dilatometric-softening point, was determined from the maximum of the dilatometric curve.

3. Results

Simple visual observations showed significant differences between different glasses in terms of color, homogeneity and transparency. These characteristics are summarized in Table 2. The color variations are clearly due to the presence of various rare-earth elements. Modified preparation procedure resulted in considerably better homogeneity of the samples compared to the earlier materials.[23–25] Core/rim zones in transparent Sc-, Y- and Nd-containing samples seem to result from different cooling rates at the surface and in the bulk, which cannot be controlled in the current furnace. The decrease in transparency in the core is assumed to be caused by higher fraction of the crystalline phases, which is, however, below the detection limit of the conventional X-ray diffraction. The existence of core/rim zones is probable also in other materials but it is not visible because these glasses were nontransparent. As indicated in Table 2, all materials but ScN24 and SmN24 were amorphous. Glass ScN24 exhibit pronounced peaks of Si_3N_4 and thortveitite, $Sc_2Si_2O_7$. Grains of crystalline phases were homogeneously distributed in the glass matrix. Relative peak intensities of crystalline samarium silicate, $Sm_2Si_2O_7$, which was detected in SmN24 are considerably lower and they were not visible by optical microscopy.

3.1. Mechanical properties

Table 2 includes also the summary of other experimental results, including density, Vickers hardness and dilatometric measurements. Density increases proportionally to atomic weight of the lanthanide and almost linearly with CFS except non-lanthanides, Sc and Y. That is because the atomic weight of these elements is considerably lower than that of lanthanides.

Fig. 1A illustrates more clearly the dependence of hardness on CFS in glasses with 20 and 24 eq.% of

Table 2
Summary of the appearance, phase composition, some mechanical and rheological properties of the studied RE–Si–Mg–O–N glasses and cationic field strength (CFS) of the corresponding rare-earth element

Glass system	Homogeneity/color transparency	X-ray	Density (g cm^{-3})	HV 0.5	$\alpha_{(22,\ 722\ °C)}$ ($\times 10^{-6}$, K^{-1})	T_g (°C)	T_L (°C)	CFS (A^{-2})
ScN20	C: brown-grey, NT; R: T	Amorphous	3.096	954±29	6.7	857	894	5.405
ScN24	C: brown-grey, NT, R: white, NT	Crystalline	3.136	1010±15	6.9	845	888	
YN20	C: brown, semi-T, R: T	Amorphous	3.545	978±17	6.8	866	916	3.703
YN24	Core: brownish, NT, Rim: T	Amorphous	3.565	1030±25	7.5	872	928	
LaN0	Milkish, semi-T	Amorphous	3.814	758±9	8.0	771	809	2.817
LaN10	Dark-green, NT	Amorphous	3.891	793±12	7.7	809	851	
LaN20	Dark-green, NT	Amorphous	3.972	900±17	7.7	839	877	
LaN22	Dark-green, NT	Amorphous	3.972	914±21	7.6	847	893	
LaN24	Dark-green, NT	Amorphous	4.013	920±17	7.5	847	893	
LaN28	Grey green, NT	Amorphous	4.046	959±9	7.1	865	923	
NdN20	C: darker violet, T, R: violet, T	Amorphous	4.098	919±19	7.9	843	888	3.105
NdN24	C: darker violet, T, R: violet, T	Amorphous	4.127	963±16	8.0	853	896	
SmN20	Black, NT	Amorphous	4.189	931±25	7.3	830	861	3.269
SmN24	Black, NT	Partially crystalline	4.216	969±26	7.5	847	889	
GdN20	Greyish green, NT	Amorphous	4.335	955±27	7.0	858	895	3.410
GdN24	Grey green, NT	Amorphous	4.390	998±16	7.2	873	919	
YbN20	Black, NT	Amorphous	4.617	984±12	6.7	834	883	3.982
YbN24	Black, NT	Amorphous	4.641	1046±16	7.2	843	892	
LuN20	Greyish green, NT	Amorphous	4.639	1003±21	6.6	870	910	4.047
LuN24	Greyish green, NT	Amorphous	4.694	1053±17	6.5	882	936	

The abbreviation of C and R, respectively is used for core/rim structure, transparent and nontransparent glasses are indicated as T or NT, respectively. Accuracy of T_g determination is estimated to be more than ±1 °C. CFS was calculated based on the valence of Z = +3 and ionic radii of oxides based on data by Shannon.[22]

nitrogen and Fig. 1B shows the dependence on nitrogen content in La-containing glasses. The hardness of Y- and lanthanide-containing glasses depends linearly on CFS and increases from HV 900 and 920 in La- to ~1000 and 1050 in Lu-doped glasses, respectively. Sc-containing glasses exhibit hardness of HV 950 and 1010, however, they do not fit the dependence. Nitrogen content increase shifts hardness toward higher values. It should be noted that the sensitivity of the hardness tests was insufficient to detect measurable differences between transparent rim and dark core zones of the corresponding samples.

3.2. Thermal expansion and glass transition temperature

The coefficients of thermal expansion in RE–Si–Mg–O–N 20 eq.% for the studied rare-earth additives are shown in Fig. 2A. As usual, α slightly increases with temperature, therefore the values of $\alpha_{(22,\ 722\ ^\circ C)}$ are greater than $\alpha_{(22,\ 522\ ^\circ C)}$. Thermal expansion coefficients decrease approximately linearly from 7.5–7.7×10^{-6} K^{-1} to 6.5–6.6×10^{-6} K^{-1} with the increase of CFS for most of the elements. Similarly as in the case of hardness measurements, Sc does not fit among other elements. The values for Nd are higher than expected from linear fits. Similar behavior was observed in the case of glasses with 24 eq.% of nitrogen. The differences between thermal expansion coefficients of glasses with 20 and 24 eq.% N are relatively small and comparable with the estimated accuracy of the measurement of around 0.1×10^{-6} K^{-1}. As a result, both small increase and decrease of α were found when nitrogen content increased. The effect of nitrogen content on α in La-containing glasses is illustrated in Fig. 2B. Thermal expansion coefficients decrease from ~7.9×10^{-6} K^{-1} to 6.8–7.1×10^{-6} K^{-1}, however, the dependence is not linear even if data scatter of ±0.1×10^{-6} K^{-1} is considered. Apparently, enhanced decrease occurs at nitrogen content of 28 eq.%. The change in a between La-containing glasses with 20 and 24 eq.% N is 0.2×10^{-6} K^{-1}, which agrees with the changes in other RE-containing glasses with the same N contents.

Glass transition temperatures and Littleton temperatures are shown in Fig. 3A and B in dependence on RE type and nitrogen content, respectively. The results are similar to hardness dependence: they increase approximately linearly when heavier lanthanide is used and Sc

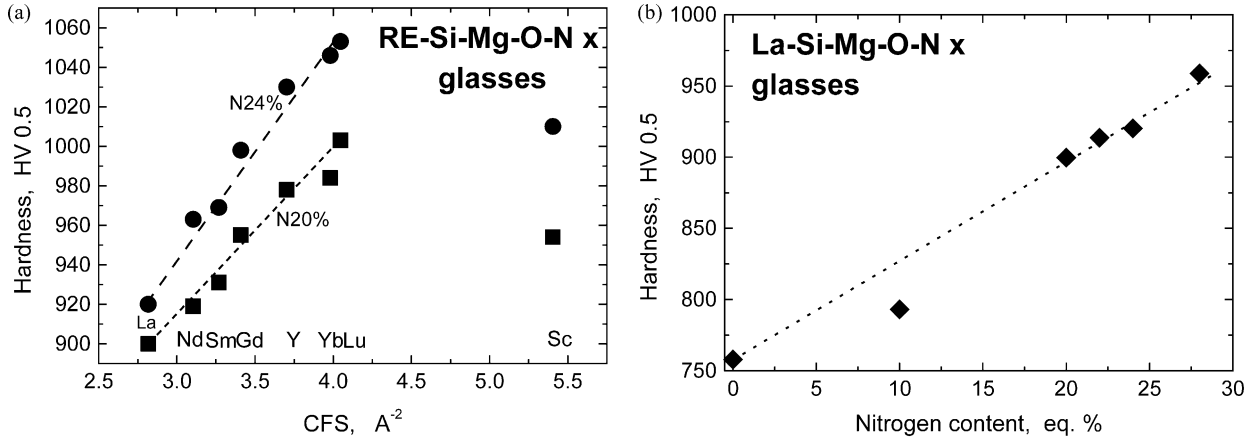

Fig. 1. Hardness dependence on cationic field strength in RE–Si–Mg–O–N glasses with 20 eq.% and 24 eq.% N and RE = Sc, Y, La, Nd, Sm, Gd, Yb, or Lu (A), and on nitrogen content in La–Si–Mg–O–N glasses (B).

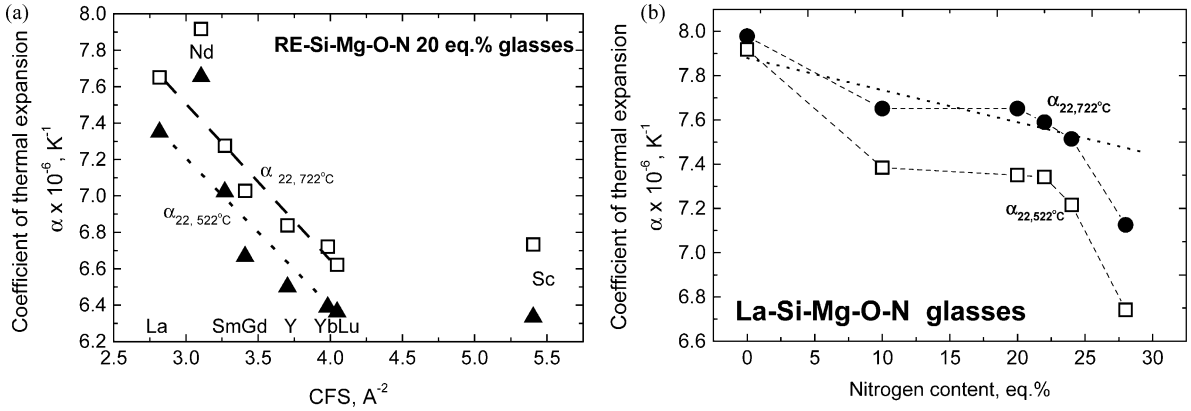

Fig. 2. Thermal expansion coefficients $\alpha_{(22,\ 522\ ^\circ C)}$ and $\alpha_{(22,\ 722\ ^\circ C)}$ of RE–Si–Mg–O–N glasses with 20 eq.% N in dependence on CFS (A), and on nitrogen content in in La–Si–Mg–O–N glasses (B).

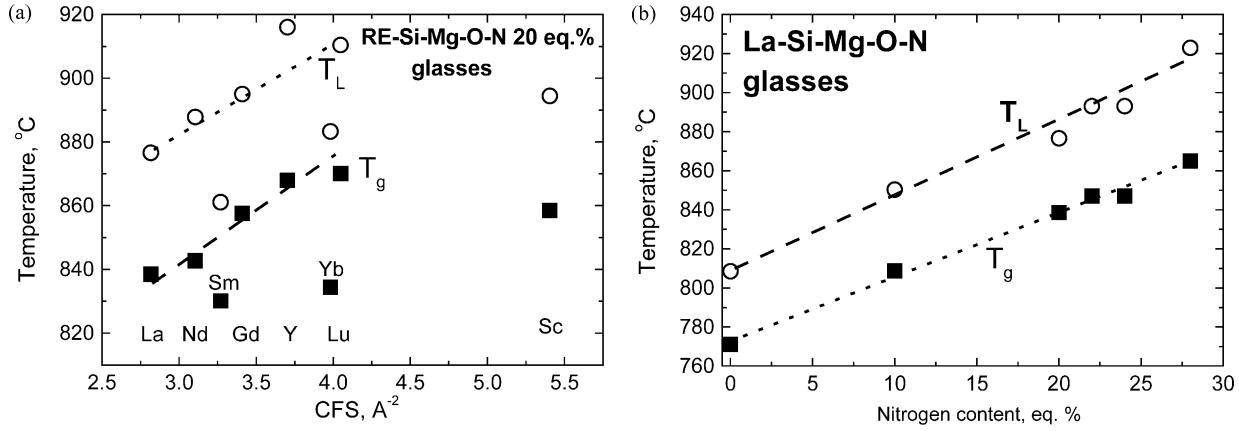

Fig. 3. CFS dependence of glass transition (T_g) and Littleton (T_L) temperatures in RE–Si–Mg–O–N glasses with 20 eq.% N (A), and their dependence on nitrogen content in La–Si–Mg–O–N glasses (B).

is the exception. T_g and T_L for Lu-doped glasses are up to 35 °C and 43 °C, respectively higher than those of La-glasses with the same nitrogen content. Transition and softening temperatures of Sc-doped glasses are similar to those of glasses with lanthanides with relatively small ionic radii between Sm and Lu. In contrast to Sc-, properties of Y-containing glasses fit well the dependence for lanthanides. The most obvious deviations and the lowest values of the characteristic temperatures were found in Yb- and slightly smaller in Sm-containing glasses. The difference between Lu- and Yb-glasses is around 36–39 °C. Nitrogen content results in linear increase in both T_g and T_L by 94 °C and 114 °C, respectively (Fig. 3B).

4. Discussion

4.1. Density vs. hardness

The results of the current study confirm relatively strong influence of rare-earth elements and nitrogen on variety of glass properties. However, these changes can relate to various phenomena, not only to the glass structure modification. For example, density increase with CFS of the lanthanide cations implies "densification" of glass structure but it overlaps with simultaneous increase of the atomic weight of corresponding lanthanides. Because of these parallel effects, the changes in glass structure due to rare-earth dopants cannot be understood only from hardness data. On the other hand, nitrogen unambiguously results in enhanced cross-linking of glass network. This is clearly demonstrated in Fig. 4. The increase of N content from 20 to 24 eq.% should cause small density decrease in RE-Si-Mg-O-N glasses since atomic weight of nitrogen is lower than that of oxygen. However, density increased by 0.5–1.3%, which is possible only due to structure "tightening". It resulted in 2.2–6.3% increase in hardness. YbN24 glass is an extreme case, when only 0.52% increase in density compared to YbN20 caused 6.3% increase in hardness. Strong effect was observed also in the case of La-containing glasses with variable N content. Its increase from 0% to 28 eq.% caused 6.1% increase in density accompanied by 26.5% increase in hardness. These values are considerably higher than the effect due to introduction of lanthanide with smaller ionic radii. For instance, substitution of La by neighboring Nd increases glass density by 3.17% but the hardness is greater only by 2.11%. When La is replaced by Lu, density increases by ~16.8–17% and hardness by 11.4–14.4%. Such differences between the changes in density and hardness can be explained only by independent and different effects of nitrogen and rare-earths on glass structure.

Fig. 4 also indicates that Sc- and Y-doped glasses are principally different from glasses with lanthanide elements. They have considerably lower densities but hardnesses comparable or slightly higher than Gd-containing glasses. Replacement of Sc by Y results in 14.5–13.7% in density increase (Sc to Y atomic weight ratio is 1.98) but only 2.5–2.0% in hardness increase, which is less than in the case of lanthanide dopants. It can be assumed that the effects of Sc and Y on glass structure are similar despite Y is often treated as one of lanthanide elements. The fact that ionic radius (and CFS) of Y lies between radii of Gd and Yb seems to be a coincidence. Thus, although hardness and some other properties of Y-glasses often fit the dependence on CFS for lanthanide-containing glasses,[13,15,17,19] Y belong into another group together with Sc. There are some experimental data supporting this conclusion. Ramesh et al.[15] reported lower hardness than predicted from linear fit in Y-containing glasses and in our earlier studies[23,24] similar deviations were found. Apparently, CFS approach applied to Sc and especially to Y, may be misleading without careful consideration of their differences from lanthanides. It is noteworthy that nitrogen influences hardness of Sc- and Y-doped glasses the same way as in the case of lanthanide containing glasses.

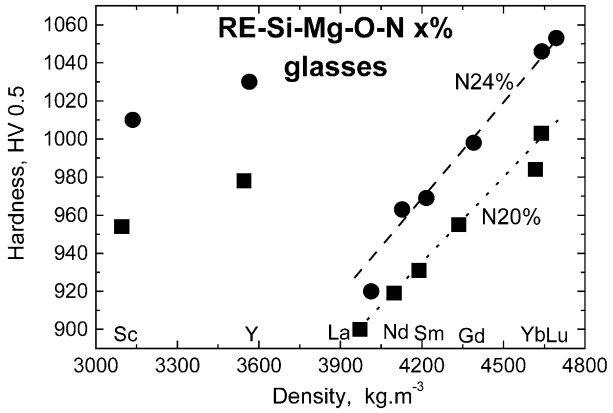

Fig. 4. Hardness vs. density in RE–Si–Mg–O–N glasses with 20 and 24 eq.% N.

The above analysis suggests that mechanisms, which are involved in rare-earth and nitrogen effects on the properties of the oxynitride glasses, are principally different. The effects of nitrogen on glass structure tightening and cross-linking are mostly linear and stronger than that of lanthanides and considerably stronger than that of lanthanides. Rare-earth elements modify the glass structure depending on dopant type. The efficiency of the lanthanide additives with regard to hardness improvement in the oxynitride glasses increases regularly from La to Lu. Sc and Y fall between Yb and Gd. Obviously, lanthanides tighten glass network via lanthanide contraction. The mechanism in the case of the dopants from III group of periodic table is questionable. However, the possible mechanisms can be considered in terms of network formers, intermediates and network modifiers. Nitrogen as network former is more effective than lanthanide network modifiers, which exhibit variations in efficiency in dependence on their size. If Sc and Y fall in the group between intermediates and network modifiers they can affect glass properties in higher or lesser extent depending on their location in the glass network.

Current conclusions are in full consent with those of Drew who more than two decades ago demonstrated that varying nitrogen and cation composition independently causes different changes in glass properties.[7] Pomeroy on Mg–Y–Si–Al–O–N glasses also showed that nitrogen and RE dopants act not only independently but their contributions add without any synergistic effect.[18]

4.2. Dilatometry

The thermal expansion of solid glasses is controlled by the asymmetry of the amplitude of thermal vibrations in the glass. It decreases as the rigidity of glass network increases. An increase of the number of non-bridging bonds would weaken the structure and increase α, whereas the changes in coordination number of network former cation may cause both its increase or decrease depending on the effect on glass structure. Nitrogen and smaller lanthanide cations tighten glass network, therefore, higher nitrogen content and lanthanides with higher atomic numbers reduce α and increase T_g and T_L in agreement with the experimental data (see Fig. 2). The arguments based on the comparison of density vs. hardness and thermal expansion changes can be used also in this case (Fig. 5A and B). Density increase of 6.1% in La-doped glasses due to the introduction of 28 eq.% nitrogen resulted in 10.7% decrease of $\alpha_{(22,722\ ^\circ C)}$ and 94 °C (~12.2%) increase in T_g, whereas an increase in density by 17% due to replacement of La by Lu decreased thermal expansion coefficients by 13% and increased T_g only by 31–35 °C (~3.5–3.2%). Again, nitrogen is more effective in modifying glass properties than rare-earth dopants.

Despite many similarities with Figs. 4, 5A and B reveal also a number of differences. Thermal expansion coefficients are higher and glass transition and Littleton temperatures in Nd-, Sm- and especially in Yb-doped glasses are lower than expected from linear dependencies (see Fig. 5A). Secondly, replacement of Sc by Y increases both α and T_g, although in all other cases a T_g increase is accompanied by a decrease of α. Finally, T_g dependence is linear while such regular behavior is not seen in α dependence (see Fig. 5B). Finally, replacement of Sc by Y increases both α and T_g, although in all other cases a T_g increase is accompanied by a decrease of α.

The reasons for enhanced effect of Nd and weakening of the effect of Yb on α, T_g and T_L are not clear. The most probable case is the change in valence at elevated temperatures since these elements can exist also as 2+ cations. Another difficulty arises when contrary effects of Y on T_g and α are considered. Detailed glass structure investigations are necessary to reveal differences between Y and other rare-earth elements. The difference between thermal expansion and T_g dependencies on nitrogen content suggest that different processes may influence glass properties at different temperatures.

4.3. Comparison with other glasses

Fair comparison of current results with other glasses is difficult because of different compositions. Density, T_g and T_L in Y–Si–Mg–Al–O–N glasses with Mg:Y ratio of 14:14 eq.%, 16 eq.% of Al and 15 eq.% of N were 3.31 g.cm^{-3}, 828 and 868 °C, respectively.[18] As expected from lower content of Mg, Y and N, these values are lower as in YN20 glass, which is the closest to this composition. RE–Si–Al—N glasses with the same content of RE (20 eq.%) and N but higher content of Al (25 eq.%),[17] exhibit 14–16% higher glass transition temperatures: 960 °C vs. 839 °C in La- and 1010 °C vs. 870 °C in current Lu-doped glasses. The thermal expansion coefficients in the same materials were around 30% lower: 5.3×10^{-6} vs. 7.7×10^{-6} K^{-1} in La-

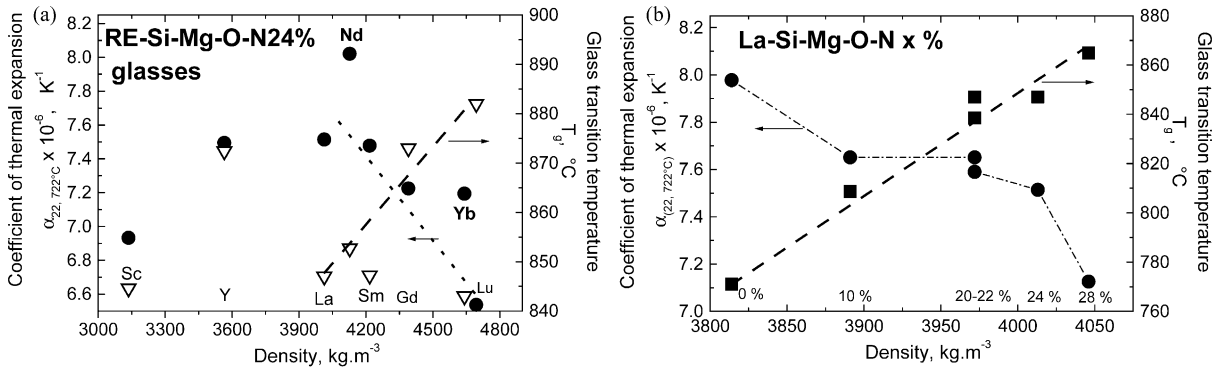

Fig. 5. The dependencies of thermal expansion coefficients and glass transition temperatures in RE–Si–Mg–O–N glasses with 24 eq.% N on their density (A), and in La–Si–Mg–O–N glasses with different nitrogen content (B).

and 4.6×10^{-6} K^{-1} vs. 6.6×10^{-6} K^{-1} in Lu-oxynitride glasses. The differences result from greater valence and coordination number of Al^{3+} than those of Mg^{2+} in glass network and from higher Al content as well.

Microhardness of Y–Si–Al–O–N glasses fitted linear dependence on CFS but their T_g behaves variably. In some cases it fits the dependence,[13,15,17,19] in others it is lower than in La–Si–Al–O–N glasses with the same nitrogen content.[27] Small deviations from linearity were visible also in the case of thermal expansion coefficients, indentation (Young's) moduli and microhardness of Y-doped Si–Al–O–N glasses but they were neglected.[17]

Deviations in behavior were earlier reported for density, hardness, T_g, and α not only in the case of Y- but also for Eu-, Gd-, Dy- and Er-doped RE–Si–Al–O–N glasses.[15,16] They were explained purely by the ionic radii change[15] or via changes of the overall glass structure by change of the dopant.[16] Since rare-earth elements included in current cover both lanthanides and non-lanthanides, wider range of property changes and possible mechanisms must be considered. Obviously, their effects cannot be described by a single dependence and without detail investigation of the changes in glass structure connected with each dopant.

5. Conclusions

Density, hardness, thermal expansion coefficients, glass transition temperatures and Littleton temperatures of RE–Si–Mg–O–N glasses can be independently modified via rare-earth additives and/or nitrogen content. Lanthanides modify hardness of the studied oxynitride glasses with 20–24 eq.% N by 11.4–14.4%, thermal expansion coefficients by ~13%, T_g by 31–35 °C and Littleton temperature by 33–43 °C. Approximately linear dependence of most properties on CFS suggests that glass structure is modified proportionally to ionic radius of corresponding lanthanide cation. However, α, T_g and T_L of Nd-, Yb- and sometimes Sm-containing glasses exhibit deviations from this dependence, which may be related to the possibility of 2+ valence state. Sc and Y additives result in properties, that are similar to or slightly better than those of Gd-containing glasses. Despite many similarities, Sc and Y belong into a group, which is different from lanthanides. Nitrogen increases hardness, T_g, T_L and decreases α of La–Si–Mg–O–N glasses linearly with the nitrogen content. The changes in glass properties are additive, depend on the type of dopants and can be explained in terms of network formers, intermediates and modifiers. Nitrogen as a network former is more effective than lanthanide modifiers, which exhibit variations in efficiency in dependence on their ionic radius.

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