Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of the European Ceramic Society 26 (2006) 2497–2501

www.elsevier.com/locate/jeurceramsoc

Mixed oxidation states of Yb and Sm in Si-Al-O-N glasses

D. de Graaf[a], S. Le Rol[b], H.T. Hintzen[a,*], L. Le Gendre[b], G. de With[a]

[a] *Laboratory of Solid-State and Materials Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands*

[b] *IUT de St-Brieux, Dpt. Science et Génie des Matériaux, IETR UMR-CNRS 6141, Université de Rennes I, BP 406, 22004, Saint Brieuc Cedex 1, France*

Received 3 July 2004; received in revised form 28 April 2005; accepted 6 May 2005

Abstract

The mechanical and optical properties of samarium and ytterbium doped Y-Si-Al-O-N glasses have been studied. It has been shown that both samarium and ytterbium undergo a reduction from the trivalent state in the raw materials to the divalent state in the glass, the degree of conversion depending on the melting time. Emission spectra of samarium containing glasses show the presence of both Sm^{3+} as well as that of Sm^{2+}, which is also reflected by the Young's modulus and density. A broad absorption band of Yb^{2+} characterizes the reflection spectra of ytterbium containing glasses, indicating a similar reduction, while a second absorption band suggests the presence of some remnant Yb^{3+}. The other properties of these glasses also appear to confirm a mixed oxidation state of Yb. These reductions have been attributed to the reducing power of chemically incorporated nitrogen (N^{3-}) in the glass matrix, as demonstrated earlier for Eu-Si-Al-O-N glasses.

Keywords: Optical properties; Glass; Sialon; Rare earth doping

1. Introduction

Oxynitride glasses in general and Ln-Si-Al-O-N glasses in particular represent an interesting class of materials with an extremely high mechanical, chemical and thermal durability which makes them a possible alternative to high-performance glasses and transparent ceramics.[1] The replacement of O^{2-} by N^{3-} leads to a more covalent, rigid glass structure, which attributes to the properties of these glasses.[2]

Several studies have also been dedicated to the effect of the lanthanide ions on the (mechanical) properties of Ln-Si-Al-O-N glasses.[3–6] These studies show that, like in aluminosilicate glasses, the main parameters influencing the glass properties are the size and valence of the cation.[7] In oxide glasses most lanthanide ions adapt a trivalent state. In oxynitride glasses the valence could be lower since the introduction of nitrogen alters the reductive potential of the glasses.[8,9]

Such a reduction has already been observed in the case of europium. The mechanical performance of Eu-Si-Al-O-N glass suggested a divalent state for europium, whereas it is trivalent in oxide glasses.[3] Detailed optical and chemical analyses showed that europium had been reduced from the trivalent state in the raw materials to the divalent state in the glasses by a chemical reaction between Eu^{3+} and the chemically incorporated nitrogen (N^{3-}).[9,10] Similar effects can play a role in the case of ytterbium and samarium, which are known to be stable in the divalent as well as the trivalent state. In previous investigations to the mechanical properties of these glasses both ions were assumed to be in the trivalent state in the glass.[3,4] However, the provided data show a small discrepancy with the data available for the other trivalent lanthanides.

The main objective of this paper is to evaluate important data, which could be related to the oxidation state of these ions. Apart from the density and the Young's modulus, the luminescence characteristics of the glasses are also studied.

Samarium and ytterbium are both luminescent ions, showing different luminescence characteristics for the divalent as compared to the trivalent state. Characteristic Sm^{3+} ($4f^5$) and Sm^{2+} ($4f^6$) transitions can be found in the red part of the visible spectrum (550–750 nm). Since the positions of the 4f levels are well known, the Sm^{3+} and Sm^{2+} $4f \rightarrow 4f$ emission lines can be easily discriminated.[11–13] Yb^{2+}($4f^{14}$) and Yb^{3+}

---

[*] Corresponding author. Tel.: +31 40 2473113; fax: +31 40 244 56 19.
E-mail address: h.t.hintzen@tue.nl (H.T. Hintzen).

0955-2219/$ – see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2005.05.010

($4f^{13}$) also have very different emission characteristics. The Yb^{2+} emission is characterized by broadband 5d → 4f emission, which can usually be found in the blue/green part of the spectrum.[14] while Yb^{3+} produces 4f → 4f line emission at approximately 900 nm.[15,16]

2. Experimental

Two series of Y-Si-Al-O-N glasses were made in which yttrium was partially replaced by either samarium or by ytterbium. The overall weighed-out composition was $Ln_xY_{(15.2-x)}Si_{14.7}Al_{8.7}O_{54}N_{7.4}$ and was varied by taking x: 0.03, 0.3, 3, 6.1, 9.1, 12.2 and 15.2. As raw materials Sm_2O_3 (REacton), Yb_2O_3 (REacton), Y_2O_3 (Sheng-Etsu), SiO_2 (CE-Minerals), Al_2O_3 (Taimei) and Si_3N_4 (Akzo Nobel, Permascand) were used. The powders were mixed in a ball mill (isopropanol, agate balls). Hereafter, the mixture was dried and placed in a hexagonal-BN powder-lined graphite crucible. The starting mixtures were heated under a nitrogen atmosphere in a vertical tube furnace at a rate of 3 °C/min to 1700 °C. After a dwell time of 1 h the glasses were quenched by rapidly extracting them from the furnace and placing them in an annealing furnace operating at 800 °C. The glasses were annealed for 1 h at this temperature in air.

The thin oxide scale, which had formed on the glass and the adhering BN were removed by grinding the surface. The glass was then cut to prepare specimens for further testing. The density of the glasses was measured using the Archimedes method in water. The Young's modulus was measured using the ultrasonic pulse-echo method on plan-parallel specimens of 2 mm thickness.

Room temperature optical measurements were performed on powdered samples using a Perkin-Elmer LS-50B photofluorospectrometer. Diffuse reflection, emission and excitations spectra were taken of the samples. The reflection measurements were done using black felt and $Ba(SO_4)$ as standards.

3. Results

3.1. Density and Young's modulus

The density measurements show a clear increase of the density for higher samarium and ytterbium contents. In the case of ytterbium the molar volume of the glass remains equal ($\rho_Y = \rho_{Yb} = 7.47\ mol/cm^3$) while the addition of samarium leads to a significant increase of the molar volume ($\rho_{Sm} = 8.74\ mol/cm^3$). The molar volume calculations are based on the weighed-out composition assuming a trivalent oxidation state for the lanthanides. In Fig. 1 the molar volume of several Ln(III)-Si-Al-O-N glasses is plotted versus the ionic radius (crystal radius[17]) of the lanthanide ion. The glasses are all prepared and measured in our own laboratory except for the Er-Si-Al-O-N glass, for which the values were derived from Ref. 4. The molar volume of the glass is a function of the ionic radius of the lanthanide ion used. However, for both ytterbium and samarium the molar volume is much larger than expected from the radius of the trivalent ions. This deviation suggests the presence of both the divalent and the trivalent state of these ions.

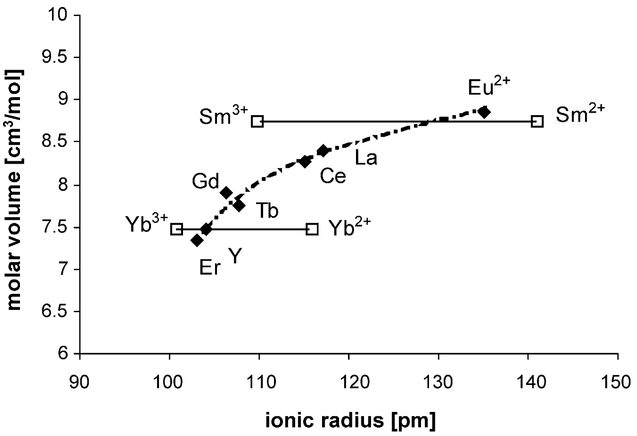

Fig. 1. Molar volume vs. ionic radius (from Ref. 17) for selected glasses with a weighed-out composition of $Ln_{15.2}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ (line serves as a guide for the eye only).

A similar behavior was observed for the Young's modulus (Fig. 2). While the other trivalent lanthanides show a systematic correlation between the Young's modulus and the ionic radius, Sm- and Yb-Si-Al-O-N glass show a deviating behavior when assuming the trivalent state and this again indicates mixed oxidation states.

3.2. Optical properties of the Sm-glasses

The reflection spectra (Fig. 3) show that the addition of samarium leads to a strong absorption over a large spectral region covering the UV and the visible part of the spectrum. The main absorption takes place in the region between 350 and 450 nm and around 550 nm, which causes the glasses

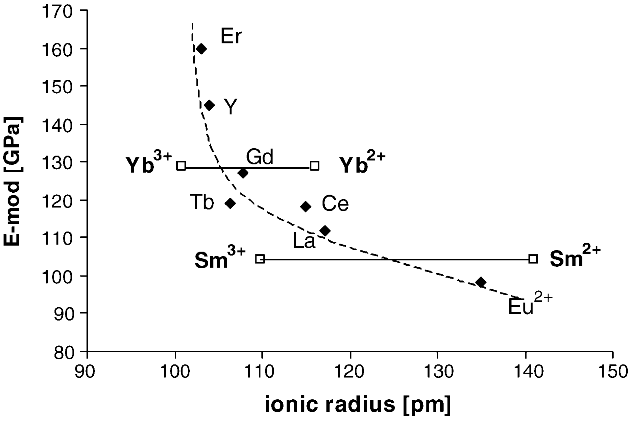

Fig. 2. E-modulus vs. ionic radius (from Ref. 17) for selected glasses with a weighed-out composition of $Ln_{15.2}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ (line serves as a guide for the eye only).

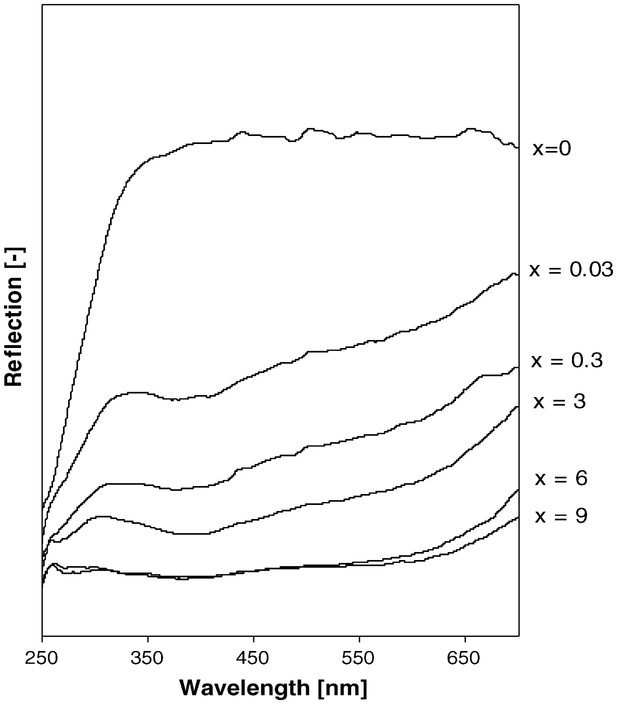

Fig. 3. Reflection spectra of powdered $Sm_xY_{(15.2-x)}$ $Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ [at%] glasses as a function of the Sm content (x).

to rapidly turn from grayish-brown to black upon samarium addition.

The emission spectra of $Sm_{0.3}Y_{14.9}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ glass (Fig. 4) clearly show the presence of both Sm^{2+} as Sm^{3+} emission lines. The excitation spectra of the same compound (Fig. 5) show a number of bands and lines, which correlate to the observed absorption maximum in the reflection spectra. The main excitation signals can be attributed to the $^6H_{5/2} \rightarrow {}^4K_{11/2}$ transition of Sm^{3+} and the $4f^6 \rightarrow 4f^55d$ transitions of Sm^{2+} (Table 1). The large excitation band at short wavelengths corresponds to the matrix absorption (Fig. 3) and can be attributed to host matrix sensitization. Because of the overlap of the excitation bands complete separation of the emission spectra is not possible. Excitation in the glass matrix leads to predominant Sm^{3+} emission whilst excitation at longer wavelengths leads to predominant Sm^{2+} emission.

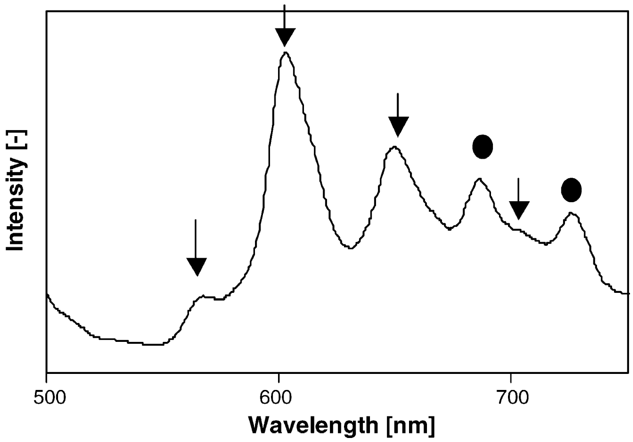

Fig. 4. Emission spectrum of a powdered $Sm_{0.3}Y_{14.9}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ glass (λ_{ex} = 404 nm). (↓) Sm^{3+} transitions, (●) Sm^{2+} transitions.

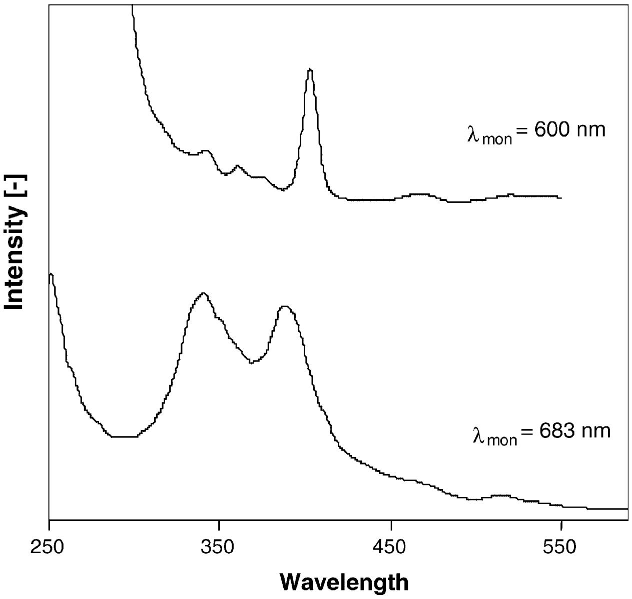

Fig. 5. Excitation spectra of $Sm_{0.3}Y_{14.9}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ glass at two different monitor wavelengths. The upper graph corresponds to the $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition of Sm^{3+} (600 nm). The lower spectrum has been taken while monitoring the $^5D_0 \rightarrow {}^7F_0$ transition of Sm^{2+} (683 nm).

Although the Sm^{3+} emission is reasonably strong at low concentrations, the emission intensity drops sharply with the concentration and no emission whatsoever can be observed at $x > 3$. This is not surprising since Sm^{3+} is very susceptible to self-quenching[18] at interatomic distances below 15–20 Å, which corresponds to Sm^{3+} contents higher than 0.1 at%.

3.3. Optical properties of the Yb-glasses

The reflection spectra of the ytterbium doped glasses (Fig. 6) show a pronounced absorption band at ~360 nm with a sideband at ~260 nm. The color of these glasses turns from yellow to brown upon ytterbium addition due to this absorption.

The characteristic 4f → 4f ground-transitions of Yb^{3+} are located at longer wavelengths than 900 nm[19] and therefore

Table 1
Observed transitions in Sm doped Y-Si-Al-O-N glass

	Excitation	(nm)	Emission	(nm)
Sm^{2+} ($4f^6$)	$^7F_0 \rightarrow 4f^55d$	340–400	$^5D_0 \rightarrow {}^7F_0$	683
			$^5D_0 \rightarrow {}^7F_1$	700
			$^5D_0 \rightarrow {}^7F_2$	725
Sm^{3+} ($4f^5$)	$^6H_{5/2} \rightarrow {}^4K_{11/2}$	404	$^4G_{5/2} \rightarrow {}^6H_{5/2}$	565
			$^4G_{5/2} \rightarrow {}^6H_{7/2}$	600
			$^4G_{5/2} \rightarrow {}^6H_{9/2}$	650
			$^4G_{5/2} \rightarrow {}^6H_{11/2}$	710

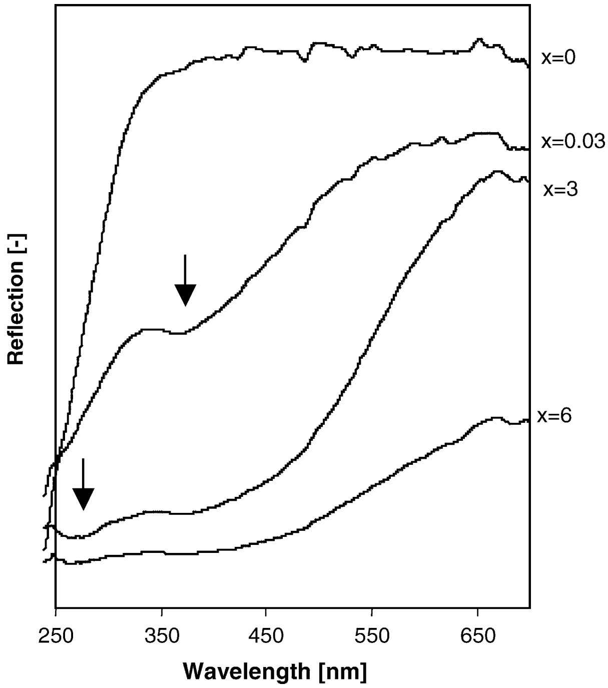

Fig. 6. Reflection spectra of $Yb_xY_{(15.2\text{-}x)}$ $Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ [at%] glasses as a function of the Yb content (*x*).

cannot lead to the coloration of the glasses. Estimation of the position of the $4f^{13} \rightarrow 4f^{12}5d$ bands of Yb^{3+} with the method of Dorenbos,[20] using the excitation spectra of Ce(III)-Si-Al-O-N glass,[21] leads to the conclusion that these bands are too far up the UV (E_{fd} (Yb^{3+}) > 70 × 10^3 cm^{-1}) to cause the observed absorption. The $4f^{13} \rightarrow 4f^{14}O^{-1}$ charge-transfer band of Yb^{3+} is usually found between 200 and 315 nm.[22,23] Therefore, we can attribute the absorption band at ~260 nm to the charge transfer transition of Yb^{3+}. However this can not explain the origin of the band at ~360 nm (28 × 10^3 cm^{-1}).

Since the observed absorption at ~360 nm cannot be originating from Yb^{3+} it suggests the presence of Yb^{2+}. This band is thus tentatively ascribed to the $4f^{14} \rightarrow 4f^{13}5d$ transitions of Yb^{2+}. The position for the $4f^{13}5d$ band of Yb^{2+} can be estimated from the position of the $4f^{6}5d$ band of Eu^{2+}, which should be approximately equal when incorporated in the same host lattice.[24] The $4f^{6}5d$ band of Eu^{2+} in $Eu_xY_{15.2-x}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ glass ($x = 0.15$) has been determined at 350 nm, which is equal to the observed absorption maximum in the Yb-doped glass at low concentrations ($x = 0.03$–0.3).[9] The absorption at longer wavelengths which becomes visible at higher Yb contents may be caused by intervalence charge transfer (IVCT) between Yb^{2+} and Yb^{3+}.[25]

Although the reflection shows the presence of a substantial amount of Yb^{2+}, no Yb^{2+} emission could be generated by excitation in the observed bands. The lack of Yb^{2+} emission is either the result of strong temperature quenching which is a common problem in Yb-doped materials,[16] or by absorption by the IVCT process.[25]

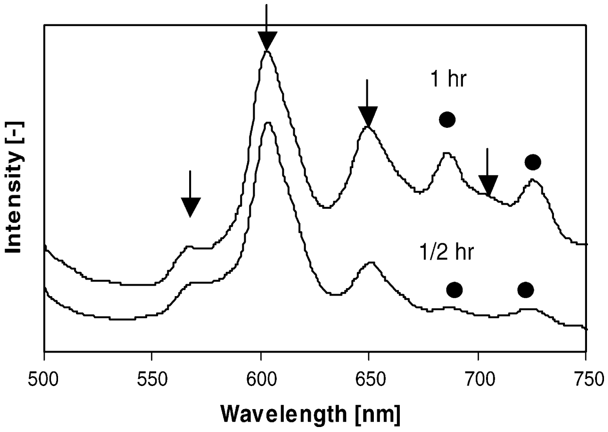

Fig. 7. Emission spectra of a $Sm_{0.3}Y_{14.9}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ glass as a function of the melting time ($\lambda_{ex} = 404$ nm). (↓) Sm^{3+} transitions, (●) Sm^{2+} transitions.

4. Discussion

From the presented results it becomes clear that both samarium and ytterbium partially reduce from the trivalent to the divalent state during the synthesis of oxynitride glasses. The reduction of Yb^{3+} and Sm^{3+} to the divalent state is less likely than that of for instance europium so that a full reduction of these ions has only been achieved in a few compounds.[26,27] However, the reduction potential of oxynitride glasses is far greater than that of oxide glasses. It has been shown in a number of studies that chemically incorporated nitrogen reacts with the lanthanides according to the following general mechanism.[9]

$$6Ln^{3+} + 2N^{3-} \rightarrow 6Ln^{2+} + N_2 \qquad (1)$$

The nitrogen gas produced by this reaction then evolves from the melt, resulting in a glass with lower content of incorporated nitrogen than expected from the weighed-out composition. For europium-containing glasses this mechanism has been validated[9] and we therefore attribute this mechanism also to the observed reactions of in Yb- and Sm-Si-Al-O-N glasses.

In previous cases a complete conversion of the lanthanide ion was observed whereas presently only a partial reduction has occurred. To look at the evolution of the Ln^{2+}/Ln^{3+} ratio with time, the glasses $Sm_{0.3}Y_{14.9}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ and $Yb_{15.2}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ were heated at shorter times (1/2 h at 1700 °C). Since the sensitivity of the reflection spectra is considered to be too low to monitor compositional variations, the Yb^{2+}/Yb^{3+} ratio is to be estimated from the mechanical properties, whereas luminescence was the ideal tool in the case of samarium. In the emission spectrum presented in Fig. 7, it can be seen that less Sm^{2+} emission is present in the sample heated for 1/2 h, as compared to the glass, which was molten for 1 h. Similarly the Young's modulus of the Yb-Si-Al-O-N glass decreases in time while the molar volume increases (Fig. 8) suggesting that the conversion of Yb^{3+} to Yb^{2+} is proceeding with time. These changes

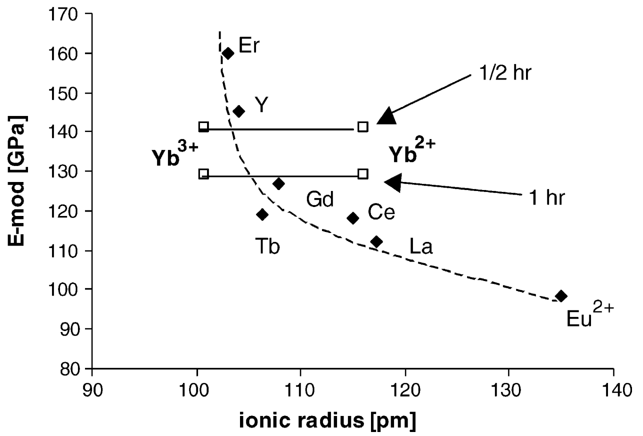

Fig. 8. E-modulus as a function of the ionic radius of selected glasses with a weighed-out composition of $Ln_{15.2}Si_{14.7}Al_{8.7}O_{54.1}N_{7.4}$ (line serves as a guide for the eye only). For Yb-Si-Al-O-N glasses the data points represent the Young's modulus after 1/2 h and 1 h melting time.

can be attributed to the replacement of Yb^{3+} by the larger Yb^{2+} and (to a lesser extent) to the decrease of the nitrogen content of the glass due to this reduction. Experiments with longer melting times were also attempted, but they led to catastrophic failure of the BN-lining and consequently to glass sticking so that these experiments were abandoned.

It goes beyond the scope of this paper to provide a detailed analysis of the reaction kinetics, but these results clearly show, that the reduction process takes place during the hottest stages of the melting process, and that the reduction itself is very slow.

This work shows that one has to be watchful for valence changes when incorporating this type of cations in (oxy)nitride systems. This is particularly the case in ceramics where lanthanides frequently are used as sintering additives and which are processed under similar conditions as these glasses.

5. Conclusions

Samarium and ytterbium partially reduce from the trivalent to the divalent oxidation state during the synthesis of Ln-Si-Al-O-N glasses (Ln = Sm, Yb). In the case of samarium this reduction has been confirmed by the presence of both Sm^{3+} as well as Sm^{2+} transitions in the emission spectrum of Sm-doped Y-Si-Al-O-N glasses and is further supported by the values of the density and Young's modulus.

For the ytterbium containing Si-Al-O-N glasses both Yb^{3+} and Yb^{2+} absorption bands were observed in the reflection spectra. Measurements on the density and Young's modulus also suggest the presence of a substantial amount of unconverted Yb^{3+}, indicating that the reduction in this case is also partial.

The reductions from Ln^{3+} to Ln^{2+} are attributed to the presence of N^{3-} in the glass melt. Increasing the melting time resulted in a variation of properties in accordance with an increasing Ln^{2+} content. This means that at this temperature, which is typical for Si-Al-O-N glass synthesis, these systems may need several hours to reach equilibrium. This dependence on the thermal history can well be the reason for the scatter in results, which are reported in literature for Sm- and Yb-Si-Al-O-N glasses.

References

1. Loehmann, R. E., *Treatise on materials science and technology, 26*. Academic press, 1985, Glass IV, p. 119–149.
2. Sakka, S., *J. Non-Cryst. Sol.*, 1995, **181**, 215–224.
3. Ramesh, R., Nestor, E., Pomeroy, M. J. and Hampshire, S., *J. Eur. Ceram. Soc.*, 1997, **17**, 1933–1939.
4. Menke, Y., Peltier-Baron, V. and Hampshire, S., *J. Non-Cryst. Sol.*, 2000, **276**, 145–150.
5. Becher, P. F., Waters, S. B., Westmoreland, C. G. and Riester, L., *J. Am. Ceram. Soc.*, 2002, **85**(4), 897–902.
6. Murakami, Y. and Yamamoto, H., *J. Ceram. Soc. Jpn. Int. Ed.*, 1994, **102**, 234–237.
7. Shelby, J. E. and Kohli, J. T., *J. Am. Ceram. Soc.*, 1990, **73**(1), 39–42.
8. Le Sauze, A., Gueguen, E. and Marchand, R., *J. Non-Cryst. Sol.*, 1997, **217**, 83–91.
9. de Graaf, D., Hintzen, H. T., Hampshire, S. and de, G., *J. Eur. Ceram. Soc.*, 2003, **23**(7), 1093–1097.
10. Hintzen, H. T., van Krevel, J. W. H., de Graaf, D., Metselaar, R., Menke, Y. and Hampshire, S., *J. Mater. Sci.*, 2004, **39**, 2237–2238.
11. Souza Filho, A. G., Mendes Filho, J., Melo, F. E. A., Custódio, M. C. C., Lebullenger, L. and Hernandes, A. C., *J. Phys. Chem. Sol.*, 2000, **61**, 1525–1542.
12. Gros, A., Gaume, F. and Gacon, J. C., *J. Sol. State. Chem.*, 1981, **36**, 324–330.
13. Patra, A., Reisfeld, R. and Minti, H., *Mater. Lett.*, 1998, **37**, 325–329.
14. Zeng, Q., Pei, Z., Wang, Z., Su, Q. and Lu, S., *Mat. Res. Bull.*, 1999, **34**(12/13), 1837–1844.
15. Zou, X. and Toratani, H., *Phys. Rev. B*, 1995, **52**(22), 15889–15897.
16. Lizzo, S., Klein Nagelvoort, E. P., Erens, R., Meijerink, A. and Blasse, G., *J. Phys. Chem. Sol.*, 1997, **58**(6), 963–968.
17. Shannon, R. D., *Acta Cryst.*, 1976, **A32**, 751–767.
18. van Uitert, L. G. and Johnson, L. F., *J. Chem. Phys.*, 1966, **44**(9), 3514–3522.
19. Dong, J., Deng, P. and Xu, J., *Opt. Mater.*, 2000, **14**, 109–113.
20. Dorenbos, P., *J. Lum.*, 2000, **91**, 91–106.
21. de Graaf, D., Hintzen, H. T. and de, G., *J. Lum.*, 2003, **104**, 131–136.
22. van Pieterson, L., Heeroma, H., de Heer, E. and Meijerink, A., *J. Lum.*, 2000, **91**, 177–193.
23. Nakazawa, E., *J. Lum.*, 2002, **100**, 89–96.
24. Verwey, J. W. M. and Blasse, G., *J. Phys. Chem. Sol.*, 1992, **53**(9), 1157–1162.
25. Kreye, M. and Becker, K. D., *Phys. Chem. Chem. Phys.*, 2003, **5**, 2283–2290.
26. von Brauer, G., Bärninghausen, H. and Schultz, N., *Zeit. für Anorg. und Allgem. Chem.*, 1967, **356**, 46–54, in German.
27. McCarty, G. J. and White, W. B., *J. Less-Common Met.*, 1970, **22**, 409–417.