

Long wavelength Eu^{2+} emission in Eu-doped Y–Si–Al–O–N glasses

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Abstract

A number of (Eu,Y)–Si–Al–O–N glasses have been prepared and their optical properties examined. Eu was found to be present in the divalent instead of in the trivalent state due to a reaction between the Eu^{3+} and the chemically incorporated N^{3-} during the preparation of the glasses. The luminescence characteristics were found to be negligibly influenced by the O/N and Si/Al ratio, but appear to be strongly dependent on the concentration and type of modifying cations (Eu,Y). As a function of the cationic composition the emission shifts from wavelengths below 500 nm to wavelengths as long as 640 nm, which is very unusual for Eu^{2+} containing compounds. This shift to longer wavelengths is ascribed to a combination of energy transfer between the different sites and change of the Eu^{2+} site distribution.

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1. Introduction

Recent investigations have shown that the incorporation of europium in nitrogen containing crystal lattices can lead to very interesting luminescence properties.¹ The direct coordination of Eu^{2+} by nitrogen leads to luminescence characteristics, which are significantly different from those that can be found in oxide environments. Examples are Eu^{2+} doped $\text{M}_2\text{Si}_5\text{N}_8$ and $\text{MSi}_7\text{N}_{10}$ (M=Ce, Sr, Ba), which display very long-wavelength emission for Eu^{2+} (> 600 nm).¹ In Ca– α –Si–Al–O–N the Eu^{2+} emission can also be found at much longer wavelengths than usual (560–590 nm instead of 350–450 nm),² while the excitation band is also located at relatively low energies. The luminescence properties, in combination with their environmental stability and low toxicity, make these materials interesting for industry. Therefore it was decided to turn our attention also to the optical properties of oxynitride glasses, a field, which is relatively unexplored.

In a previous investigation the europium was found to be present in the divalent form in Eu-doped Y–Si–Al–O–N

glasses.³ In the present study the effect of the glass composition on the Eu^{2+} luminescence is being investigated. In most M-Sialon systems, such as the Y–Si–Al–O–N system, a considerable glass-forming region can be found at a low nitrogen to oxygen ratio. The composition $\text{Y}_{35}\text{Si}_{45}\text{Al}_{20}\text{O}_{83}\text{N}_{17}$ (equivalent%) has been chosen as a central point since this composition has been reported to yield the B-phase upon crystallisation.^{4–6} In this composition a variable amount of yttrium was replaced by europium to act as an activator cation. The composition was further varied along the three axes which are defined by the: (Eu,Y)/Al, Si/Al and O/N ratio.

2. Experimental

2.1. Preparation and characterisation of the glasses

The compositions of the starting mixtures that have been weighed-out in this investigation are listed in Table 1. Eu_2O_3 (99.9% Rare-earth Products Ltd.), Y_2O_3 (99.9% Rare-earth Products Ltd), SiO_2 (Fluka Chemicals Ltd.), Al_2O_3 (BDH laboratory supplies) and Si_3N_4 (Starck) were taken as raw materials. All oxides were calcined at 900 °C to remove any volatiles and/or

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Table 1
Weighed-out compositions of the investigated glasses

Code	Eu (at.%)	Y (at.%)	Si (at.%)	Al (at.%)	O (at.%)	N (at.%)
S1G1	0.15	15.0	14.7	8.7	54.1	7.4
G1	1.5	13.7	14.7	8.7	54.1	7.4
S1G2	9.1	6.1	14.7	8.7	54.1	7.4
S2G1	1.8	16.0	14.7	6.1	54.1	7.4
G1	1.5	13.7	14.7	8.7	54.1	7.4
S2G2	1.0	8.8	14.6	14.3	54.0	7.4
S3G1	1.5	13.8	18.5	4.0	54.7	7.4
S3G2	1.5	13.8	16.7	6.1	54.4	7.4
G1	1.5	13.7	14.7	8.7	54.1	7.4
S3G3	1.5	13.4	10.6	14.1	53.1	7.3
S4G1	1.5	13.3	14.3	8.5	60.3	2.1
S4G2	1.5	13.5	14.4	8.6	57.8	4.3
G1	1.5	13.7	14.7	8.7	54.1	7.4

chemically absorbed water. A homogeneous powder was obtained by ball-milling the powder mixture overnight in iso-propanol with Si₃N₄ balls and subsequently drying it. The powder was iso-statically compressed (dry-bag, 150 MPa) to a pellet of 50 g. The pellet was melted in a vertical tube furnace at temperatures between 1700 and 1750 °C, depending on the glass composition. Melting was performed in a nitrogen atmosphere. The carbon crucible was lined on the inner wall with Hex-BN powder to prevent sticking. The melt was quenched by pouring it in a graphite mould, which was pre-heated at 800 °C and subsequently annealed for two hours at this temperature in air. The glasses were

determined to be X-ray amorphous. The nitrogen content of selected glasses was determined using LECO O/N analysis.

2.2. Optical measurements

The glasses were cut in sheets of 500 µm thickness which were polished with a 10 µm diamond disk. UV-Vis transmission spectra were taken of these samples in the range of 200–900 nm, using a Shimadzu PC-2401 Spectrophotometer equipped with an integrating sphere assembly. Luminescence measurements were performed on bulk samples using a Perkin-Elmer LS-50B spectrofluorometer equipped with a Xenon flash-lamp.

3. Results and discussion

3.1. The reduction of europium

The emission spectra show only broadband emission (Fig. 1 a), which is consistent with our previous observation that Eu³⁺ in the raw materials will reduce to Eu²⁺ in the glasses.³ Only Eu²⁺ can give broadband emission whilst the electronic structure of Eu³⁺ yields line emission at well-defined wavelengths (Fig. 1b). No evidence was found for the presence of Eu³⁺ emission or absorption. Therefore the reduction is assumed to take place by a mechanism similar to that which has been proposed for Cu²⁺ reduction in phosphorus oxynitride glasses, given by the following general equation:⁷

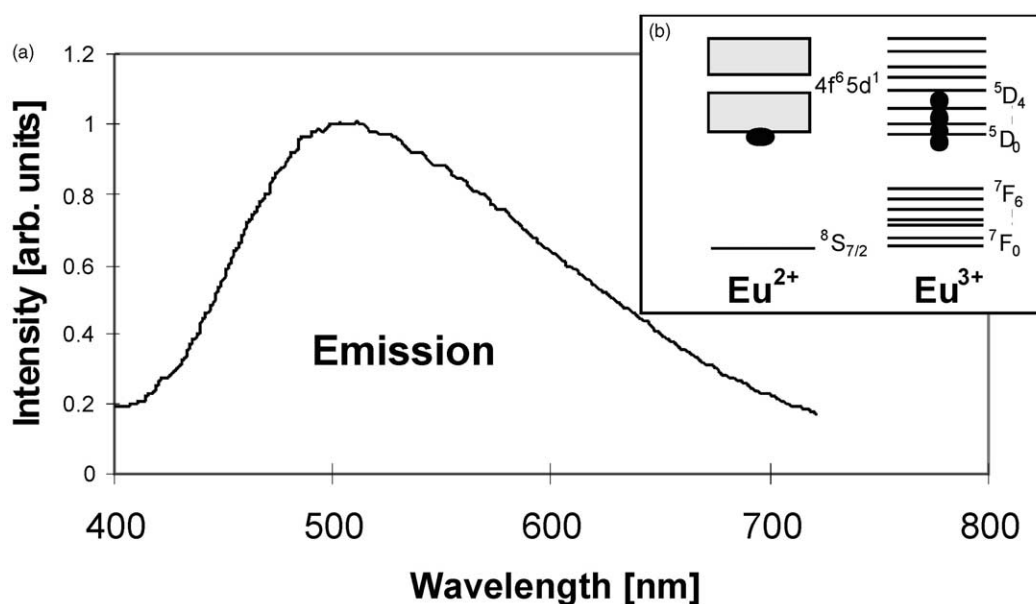
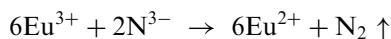


Fig. 1. (a) Broadband emission in a glass with the composition S1G1, (b) energy levels in Eu²⁺ and Eu³⁺, ● emitting levels.

This mechanism implies a reduction of the nitrogen content of the glasses as compared to the weighed-out composition. Measurements of the actual nitrogen content by means of LECO O/N analysis show that this indeed is the case (Fig. 2). The difference between the weighed-out nitrogen content and the measured nitrogen content increases with increasing europium content, which is expected if the above mechanism is valid. Moreover the measured nitrogen content can be closely related to the calculated nitrogen content, based on the weighed-out composition and assuming a full reduction of Eu^{3+} . Based on the spectroscopic evidence and the results of the nitrogen analysis we conclude that the reduction of Eu^{3+} indeed occurs and can be considered to be nearly complete.

The implication of this reaction for the structure of the glass is a decrease of the network connectivity as the nitrogen content decreases. Combined with the larger ionic radius and lower valence of Eu^{2+} as compared to Eu^{3+} this will lead to a considerable lower mechanical performance than expected when europium were to be in the trivalent state, as has been experimentally verified by Ramesh et al.⁸

3.2. Absorption by Eu^{2+}

Undoped Y–Si–Al–O–N glasses are reported to be colourless,^{5,9} in contrast to the Eu-doped ones.

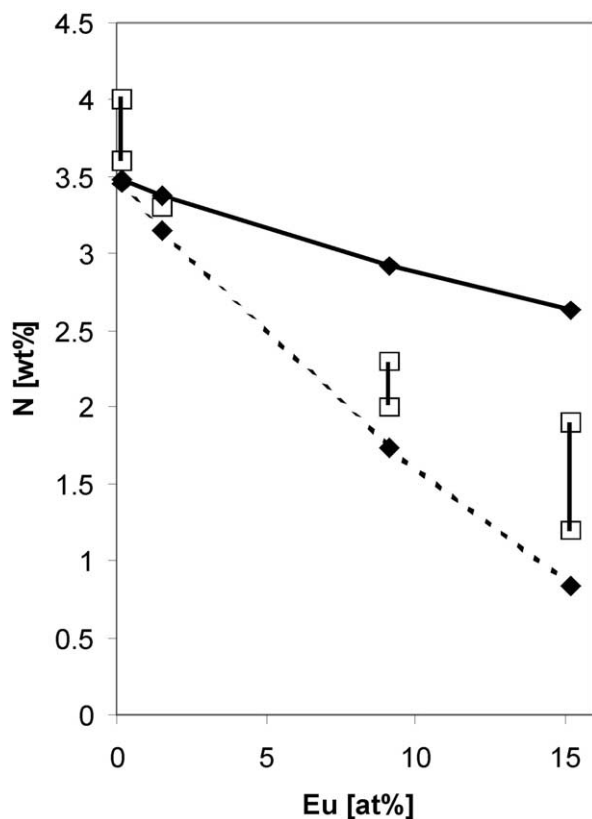


Fig. 2. Nitrogen content: weighed-out (—◆—), expected for a complete conversion (-◆-) and measured by LECO (□).

Depending on the europium content of the glasses the colour can range from green (low Eu-content) to amber (high Eu-content). This is reflected by the UV–Vis spectra (Fig. 3). This figure also shows, that the absorption of these glasses is relatively insensitive to compositional changes other than to the change of the europium content. Indicated in the spectra is the absorption band, which can be assigned to europium. With increasing europium content this band grows and shifts to longer wavelengths thus shifting the absorbing region to longer wavelengths and reducing the transmission at short wavelengths.

3.3. The dependence of Eu^{2+} emission and excitation on the glass composition

Both the series with a varying Si/Al ratio and a varying O/N ratio show no significant change of the position of the emission and excitation band, which are located at approximately 430 and 600 nm respectively. This indicates that nitrogen for this overall composition is not directly coordinated with europium in contrast to many crystalline oxynitrides^{1,2} but this is in accordance with claims that nitrogen in M–Si–Al–O–N glasses of similar composition only performs a bridging function between three silicon atoms.¹⁰ This needs not to be necessarily true for other compositions, which lie outside the compositional range measured in this study, since a significant amount of non-bridging nitrogen ($=\text{N}$ and N^{2-}) has been found in Na–Si–O–N glasses.^{11,12} For the investigated compositions it can be concluded that charge compensation is predominantly delivered by non-bridging oxygen ($-\text{O}^-$) and/or aluminium.

Strong changes of the luminescence characteristics were found by changing the Eu/Y ratio. With increasing Eu-content the low-energy edge of the excitation band is extended towards longer wavelengths (Fig. 4), which corresponds with the shift of the absorption edge in the UV–Vis spectra. The emission also undergoes a shift to longer wavelengths with increasing Eu-contents (Fig. 5). For the concentration range, which has been used in this investigation (0.15–9.2 at.% Eu) the emission shifts from 500 to 640 nm.

A similar effect occurs when altering the (Eu,Y)/Al ratio (series 2). In this series the wavelength of the Eu^{2+} emission increases with increasing (Eu,Y)/Al ratio. In Fig. 6 the energy of the emission maximum is plotted against the Eu-content for the glasses of series 1 and 2. The position of the emission band appears to be primarily dependent on the concentration of europium, while there is a minor influence of yttrium.

Energy transfer, where a Eu^{2+} site is excited and subsequently donates its energy to a neighbouring Eu^{2+} site, can explain the strong shift of the emission to longer wavelengths and its dependence on the Eu^{2+} concentration. Of course this can only occur if the excited state of

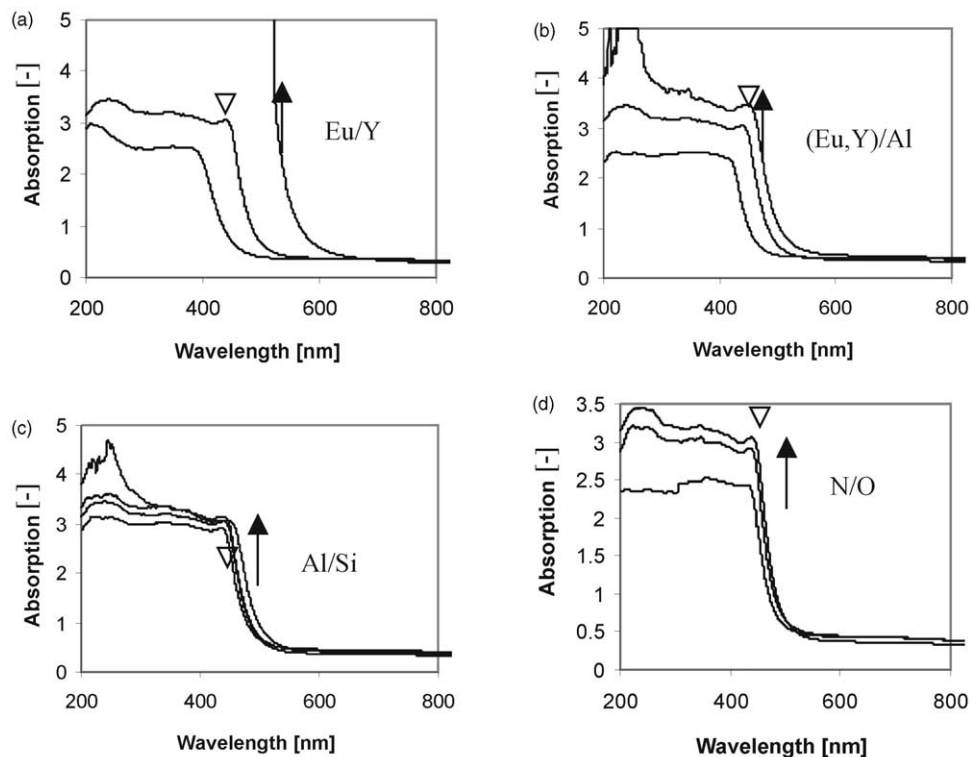


Fig. 3. UV-Vis transmission spectra of Eu-Y-Si-Al-O-N glasses with a varying: (A) Eu/Y ratio (Series 1), (B) (Eu,Y)/Al ratio (Series 2), (C) Al/Si ratio (Series 3), (D) N/O Ratio (Series 4), ∇ Eu^{2+} absorption band.

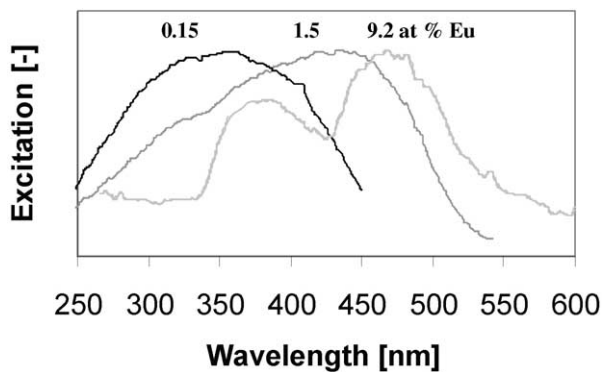


Fig. 4. Excitation bands as a function of the Eu/Y ratio (Series 1).

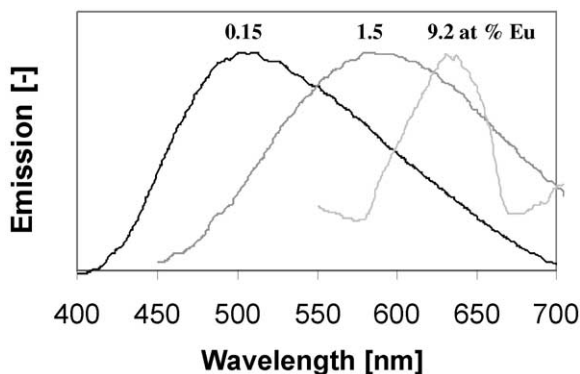


Fig. 5. Emission bands as a function of the Eu/Y ratio (Series 1).

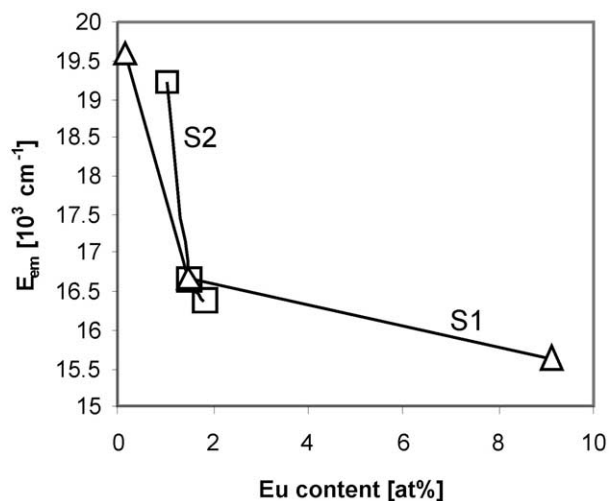


Fig. 6. Emission energy as a function of the Eu-content for the glasses of series 1 [Eu/Y] and 2 [(Eu,Y)/Al].

the receiving Eu^{2+} ion is located at lower energies than that of the donating ion. This is the case in glasses where a distribution of Eu^{2+} sites is present rather than one well-defined site. The probability of energy transfer between two ions increases as the distance between the donor and the acceptor ion decreases, which is in accordance with the observed dependence of the emission energy on the Eu^{2+} concentration.

Table 2
Emission wavelength as a function of the excitation wavelength and the glass composition

Glass	Eu (at. %)	λ_{em} (nm)			
		$\lambda_{ex}=300$ (nm)	$\lambda_{ex}=350$ (nm)	$\lambda_{ex}=400$ (nm)	$\lambda_{ex}=450$ (nm)
S1G1	0.15	505	510 ^a	540	540
G1	1.52	590	590	600 ^a	625
S1G2	9.12	610	630	640	640 ^a
S2G2	1.0	510	520 ^a	525	550
G1	1.5	590	590	600 ^a	625
S2G1	1.8	605	610	610 ^a	620

^a Maximum emission intensity.

Apart from the fact that energy transfer is a logical explanation for the emission shift, the existence of the low-energy emitting sites indicates a very special Eu^{2+} coordination. The fact that it is not possible to produce long-wavelength emission at low Eu^{2+} contents (Table 2), suggests that these sites are only formed at higher Eu^{2+} contents. Evidently, at high Eu^{2+} contents, part of the Eu^{2+} ions experience a large nephelauxetic effect and a large ligand field due to incorporation on a small covalent site,¹³ the nature of which is a point for further research.

4. Conclusions

Eu^{3+} in the starting materials of (Eu,Y)–Si–Al–O–N glasses is reduced to its divalent form by a reaction with the chemically incorporated nitrogen. The luminescence characteristics of these glasses appear to be only marginally dependent on the network forming cations and anions, but strongly on the concentration and type of network modifying cations (Eu,Y). By a variation of the cationic composition the emission can be shifted over a large interval 500–650 nm, while the excitation also shifts to long wavelengths. The concentration dependence of the emission and excitation wavelengths can be explained by assuming a changing site distribution and energy transfer between the different sites.

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