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Evidence for the presence of Eu^{2+} in (Y,Eu)-Si-Al-O-N glass by luminescence spectroscopy

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During recent years intensive research has been carried out on Si-Al-O-N glasses [1]. Two reasons can be given for this interest. Firstly, glassy Si-Al-O-N phases are formed at the grain boundaries of Si_3N_4 ceramics when densified by liquid phase sintering applying metal oxides as additives. The resulting amorphous phases dominate the high temperature properties, and for this purpose glasses are of interest, which can be crystallized easily. Secondly, oxynitride glasses show improved corrosion and mechanical properties compared to oxide glasses [2]. A few years ago, one of the current authors reported an extensive study to the influence of the rare-earth ion on the mechanical properties of Ln-Si-Al-O-N glasses (Ln = Y, Ce, Nd, Sm, Eu, Dy, Ho, Er) [3]. A systematic relationship between several properties and the ionic radius of the Ln ion was found, except for Eu. This triggered the research on the luminescence properties of the Eu doped Si-Al-O-N glasses with the intention to get more information about the valency of the Eu ion. By measurement of the emission spectra the divalent state can unambiguously be discriminated from the trivalent state.

For this study an (Y,Eu)-Si-Al-O-N glass was selected with the weighed-out composition $Eu_{0.04}Y_{12.26}Si_{18.5}Al_7O_{54.7}N_{7.5}$. A mixture of Y_2O_3 (99.9%, Rare Earth Products Ltd.), Eu_2O_3 (99.9%, Rare Earth Products Ltd.), SiO_2 (Fluka Chemicals Ltd.), Al_2O_3 (BDH laboratory supplies) and Si_3N_4 (Starck, LC12SX) was heated at 1700 °C in a nitrogen atmosphere, after which the melt was cast into a graphite mold at 850 °C. Details about the composition and preparation conditions are given in [3]. The luminescence measurements were performed at room temperature with a Perkin-Elmer LS50B spectrophotometer in the same way as described previously [4].

The emission spectrum of the (Y,Eu)-Si-Al-O-N glass (Fig. 1) clearly shows a band centered around 450 nm, which is typical for transitions from the 5d to the 4f level of divalent Eu [5]. Sharp lines around 610–615 nm, characteristic for the 4f → 4f transitions of trivalent Eu [5], were not observed. Therefore it can be concluded that Eu is present in the divalent state, and that Eu^{3+} can only be present in minor amounts. The fact that Eu^{2+} is present explains the deviating behavior of the Eu-Si-Al-O-N glass with respect to the mechanical properties as compared to the other Ln-Si-Al-O-N (Ln = Y, Ce, Nd, Sm, Dy, Ho, Er) glasses for which the Ln ions are present in the trivalent state [3]. The larger ionic radius of Eu^{2+} as compared to that of Eu^{3+} [6] leads to a reduction of the rigidity of the glass matrix and henceforth to a decrease of mechanical properties such as the hardness and the Young's modulus.

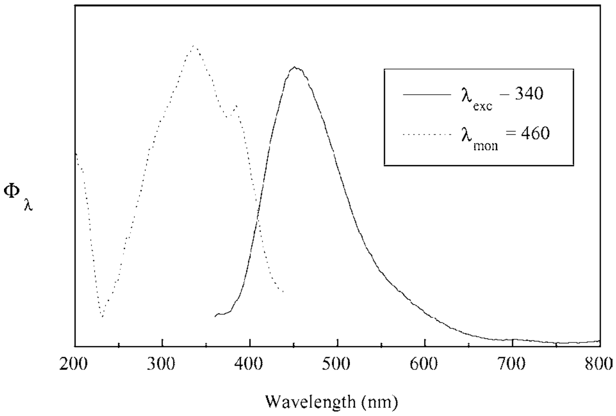

Figure 1 Emission and excitation spectrum of the glass with weighed-out composition $Eu_{0.04}Y_{12.26}Si_{18.5}Al_7O_{54.7}N_{7.5}$. The peak at about 385 nm in the excitation spectrum is an artifact due to the measurement procedure.

As the glass was prepared starting with trivalent Eu (Eu_2O_3), we feel that the reduction to Eu^{2+} is related to the reducing behavior of the oxynitride matrix, which was nicely demonstrated by the work of Marchand *et al.* at phosphorus oxynitride systems [7]. By determination of the nitrogen content of the resulting oxynitride matrix the suggested mechanism was proved [8], and quantification of the Eu^{2+} and Eu^{3+} content was done by magnetic measurements [9].

The band width of the Eu^{2+} emission is about 5000–6000 cm^{-1}, which is about the same halfwidth as observed for Eu^{2+} present on a single site in crystalline silicate and aluminate materials (5000–6000 cm^{-1} [10, 11]). In addition, the emission spectrum hardly changes for varying excitation wavelengths. This indicates that for the low Eu concentration used the site on which Eu is incorporated in the amorphous glass matrix is rather well defined, or in other words, the site distribution always present in glasses is rather narrow. The Stokes shift, as estimated from the positions of

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the emission band and the excitation band (Fig. 1), is 7000–8000 cm^{-1}, which is in the range of values which can be calculated for Eu^{2+} doped SiO_2 and Al_2O_3-SiO_2 glasses (7000–10 000 cm^{-1} [12]).

With luminescence spectroscopy it has been shown that in (Y,Eu)-Si-Al-O-N glass Eu is present as a divalent ion, which for low Eu concentrations is incorporated on a quite well defined site. This explains the deviating behavior of the Eu-Si-Al-O-N glass with respect to mechanical properties of Ln-Si-Al-O-N glasses in which the lanthanide ion Ln is present in the trivalent state.

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