Spectroscopic analysis of a Eu-doped aluminosilicate optical fiber preform

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An optical fiber whose core is an aluminosilicate glass doped with Eu 3+ and Eu 2+ ions has been made using modified chemical vapor deposition and a novel aerosol delivery technique. The UV-visible absorption of the preform has been studied in the 200-700 nm range as well as the excitation and emission spectra between 230 and 720 nm. Three broad UV absorption bands with maxima at 255, 302 and 316 nm have been observed. The relative intensities of fluorescent and the transition probabilities from the 5D 0 levels of Eu 3+ in the preform were compared with those of phosphosilicate and germanate glasses. For Eu 3+ emission, a linear relation between excitation and maximum emission wavelength has been observed as excitation wavelength increases beyond 375 nm. Infrared absorption spectra were also analyzed for the preform.

1. Introduction

We have fabricated a Eu-doped preform and fiber using modified chemical vapor deposition (MCVD) in conjunction with a novel aerosol delivery technique [1]. Several other methods have been developed to incorporate rare earth ions in optical fiber cores due to the low vapor pressure of rare earth compounds. These are solution doping [2,3] and volatile halide methods [4]. We believe the aerosol delivery technique [1] possesses several advantages, i.e., ease of application, minimal use of precursors (20-30 ml), efficient structuring of the radial index profile as well as low OH - content.

Recently, photosensitivity [5,6] and second harmonic generation [7] were observed in Ge-free rare earth-doped fibers. A Eu-doped fiber has shown an index change of 10 -5 when irradiated by a KrF excimer laser (249 nm) [5]. Photosensitivity has been mainly observed in germanosilicate fibers using laser irradiation at 488 nm and 245 nm [8,9]. Even though the mechanism of this phenomenon is not completely understood, the index change has been attributed to photo bleaching of the strong GeO absorption band at 244 nm [10]. Photosensitivity has been also reported in Eu 3+-doped bulk glasses at the 465 nm Ar ion laser line resonantly tuned to 3 F 0 → 2 D 2 transition of the ion [11]. This phenomenon was explained in terms of a structural change caused by thermal relaxation between 5 D 2 and 5 D 0 levels of the Eu 3+ ion.

The origin of photosensitivity in the UV of this germanium-free Eu-doped fiber cannot be explained either by mechanisms present in germanosilicate fibers or by that of Eu 3+-doped glasses. We anticipate that spectroscopic studies of our Eu-doped fiber preform and a comparison with germano-silicate glasses will lead to a better understanding of photosensitivity.

In the following, we describe the fabrication and characterization of a Eu-doped aluminosilicate preform and fiber. Spatially resolved UV-visible absorption spectra of the preform and the
attenuation spectra of the fiber have been measured to aid in understanding the origin of UV photosensitivity of the fiber. The excitation and emission spectra of the preform were measured to analyze valence states of Eu ions and their spectroscopic characteristics in the glass. The site symmetry of the glass structure around the Eu\(^{3+}\) ion in the preform was also inferred from the spectra, and the structure of the glass made by MCVD with an aerosol delivery technique was compared with those of glasses made by melting. Detailed IR spectra were taken to study the glass structure of the preform by vibrational mode analysis.

2. Fabrication and sample preparation

The fabrication process cited above is shown schematically in fig. 1. Twelve cladding layers were formed by conventional MCVD using SiCl\(_4\) and POCl\(_3\) on a Heraeus Amersil Heralux tube. The two core layers were formed using only aerosol deposition. An organometallic solution, described below, was nebulized with a 1.5 MHz transducer and transported with He as a carrier gas into an MCVD substrate tube. The composition of the organometallic solution was as follows: 8.0 ml TEOS (tetraethyl orthosilicate), 3.0 ml Al(OBu)\(_3\) (aluminium-tri-sec-butoxide), 0.4 ml PO(OBu)\(_3\) (tributyl-phosphate), 0.3 g Eu(tmhd)\(_3\) (2,2,6,6-tetramethyl-3,5-heptanedionato europium) dissolved in 5 ml Cl\(_2\)BrC (bromo-trichloromethane) and 12 ml MEA (methoxy-ethylacetate). The formation of a very fine white powder was observed at a relatively low temperature around 350°C (measured at the outside of the substrate tube). The powder was a multicomponent oxide soot produced from metallic precursors. The organic rest left the reaction zone as vapor. As the temperature increased above 350°C, carbon formation caused by the pyrolysis of the organic rest darkened the oxides. The formation of amorphous multicomponent oxides from these precursors was observed at relatively low temperature in the absence of oxygen. A high temperature reaction was chosen to increase thermophoretic efficiency, and the removal of carbon and OH\(^-\) was carried out as follows. The soot was dehydrated at 1200°C on the MCVD lathe and using oxygen and the carbon was burned to CO\(_2\) at 1350°C. The removal of carbon in the glass was confirmed by IR spectra discussed below. The soot was then sintered with two passes of the torch with the temperatures at 1500°C and 1900°C. Finally, the substrate tube was collapsed into a fiber preform at 2100°C. A detailed de-

![Fig. 1. Schematic of MCVD with an aerosol delivery technique.](image-url)
The preform diameter was 14.2 mm with a core diameter of 1 mm. A section of preform was cut longitudinally into a slab and polished for spectroscopic measurements. The final sample size was $15 \times 14.2 \times 0.55$ mm$^3$ with a 1 mm wide core. The remainder of the preform was drawn into 122 $\mu$m fiber with a core diameter of 8.6 $\mu$m. The difference between the core and the cladding indices was $\Delta n = 0.0025 \pm 0.0001$, and the index profile of the fiber is shown in fig. 2. The composition of the core was determined by wavelength dispersive X-ray microprobe analysis, and the average weight percent is given as follows: 93.74% SiO$_2$, 4.9% Al$_2$O$_3$, 0.7% P$_2$O$_5$, 0.1% Eu$_2$O$_3$, = 0.5% EuO. The analysis provided the total concentration of all europium ions. The concentration of Eu$_2$O$_3$ (Eu$^{3+}$) was determined separately by comparing the emission and excitation spectra of the preform with those of a Eu$^{3+}$-doped alkaline silicate glass provided by J.T. Kohli of Schott Glass Technology. This Eu$^{3+}$-doped alkaline silicate glass had a composition in weight percent as follows: 0.99% Eu$_2$O$_3$, 2.99% LiO$_2$, 7.23% Na$_2$O, 4.71% K$_2$O, 84.08% SiO$_2$.

3. Data and results

3.1. UV–visible absorption spectra

The energy levels of Eu$^{2+}$ and Eu$^{3+}$ ions in crystals are shown in fig. 3. For the Eu$^{3+}$ ion, the $4f^7 \rightarrow 4f^65d^1$ transitions are electric dipole allowed, producing blue–green fluorescence with a broad bandwidth and high luminescence output [12].

In Eu$^{3+}$, the transitions are within the 4f shell and produce orange–red luminescence. These are allowed magnetic dipole transitions and forced electric dipole transitions [13]. The dark circles indicate the levels from which emission occurs and less probable transitions are shown as open circles. In Eu$^{2+}$ ions, the $4f^65d^1$ level is split into $e_g$ and $t_{2g}$ levels by a cubic crystal field [14]. The Eu$^{3+}$ ion energy levels are shown and include a charge transfer state (CTS) as well as $f \leftrightarrow f$ transitions. In the case of oxide glass hosts, the CTS is caused by an electron jumping from surrounding oxygen atoms to a partly filled f shell of the Eu$^{3+}$ ion [13].

The spatially resolved absorption spectra of the preform sample were measured in the 200–700 nm range with a Perkin–Elmer 552 UV–VIS
spectrophotometer and the results are shown in fig. 4. The spectra were taken from both the core center and the core-cladding interface using a micropositioner to translate the sample. At the center of the core, two absorption bands centered at 255 nm and 302 nm were observed as well as a 316 nm band at the shoulder of the 302 nm band. As the probed position was moved toward the core-cladding interface, the resolution of the three UV peaks increased; however, their intensities decreased. Because of the small absorption length (0.55 mm) of the sample, the weak absorption bands of Eu$^{3+}$ in the visible range were not detected and are not shown in fig. 4. However, these were apparent in the fiber where the attenuation was measured using a cut-back method (from 10 to 3 m) with an optical spectrum analyzer (Ando AQ6312B). In this measurement, the absorption peaks of Eu$^{3+}$ were well resolved. The spectrum in fig. 5 is consistent with the excitation spectra in fig. 6. Based on the reported data [14], the 255 and 316 nm bands are assigned
Fig. 4. Absorption spectra of the core and the core-cladding interface of the preform described in the text, in the 200–700 nm region.

to the $4f^7 \rightarrow 4f^65d^1(t_{2g})$ and $4f^7 \rightarrow 4f^65d^1(e_g)$ transitions of Eu$^{2+}$ respectively. The 302 nm band is associated with energy transfer from Eu$^{3+}$ to Eu$^{2+}$ based on the observation in the excitation spectra discussed in the following sections.

3.2. Excitation and emission spectra

The excitation and emission spectra of the preform core were measured using a Spec DM3000F monochromator with a Xenon lamp whose minimum bandwidth is 0.36 nm. The excitation spectra were monitored with emission at 422 nm and 616.5 nm, which correspond to the $4f^65d^1(e_g) \rightarrow 4f^7$ transition of Eu$^{2+}$ and the $5D_0 \rightarrow 7F_2$ transition of Eu$^{3+}$. The results are shown in fig. 6. For the excitation spectrum of Eu$^{2+}$ ion, the $4f^7 \rightarrow 4f^65d^1(e_g)$ transition band centered at 316 nm was observed. The Eu$^{3+}$ excitation spectrum showed another broad absorption band cen-

Fig. 5. Attenuation spectrum of the fiber drawn from the preform, the spectrum of which is shown in fig. 4.
Fig. 6. Excitation spectra of Eu ions in the preform. Note that the maximum of the $4f^25d^1(e_g) \rightarrow 4f^7$ emission band at 422 nm was monitored for Eu$^{+2}$ ions and that of the $^7D_0 \rightarrow ^7F_2$ emission band at 616.5 nm was monitored for Eu$^{+3}$ ions.

tered at 302 nm in addition to sharp f $\rightarrow$ f transitions.

We also have measured the excitation spectrum for a Eu$^{+3}$-doped alkaline silicate glass provided by Schott Glass Technology. This glass had a Eu$^{+3}$ concentration of 0.99 wt%, and Eu$^{+2}$ ions were not present. The excitation spectra were taken for the emission at 610 nm, the maximum in the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{+3}$ in this glass. The excitation spectra of Eu$^{+3}$ ions permitted a comparison of both glasses so that the study of the behavior of Eu$^{+3}$ in the presence of Eu$^{+2}$

Fig. 7. Comparison of excitation spectra of Eu$^{+3}$ ion in the preform and an alkaline silicate glass. Here the maximum of the $^5D_0 \rightarrow ^7F_2$ emission was monitored. It occurred at 616.5 nm in the preform and 610 nm in the alkaline silicate glass.
ions may be carried out. The excitation spectra of Eu$^{3+}$ in both preform and the alkaline silicate glass are shown in fig. 7. The broad band near 302 nm was observed in the preform; however, in the alkaline silicate, this was absent. The band at 302 nm in the preform appeared to be a superposition of sharp UV lines of Eu$^{3+}$ superimposed on the broad $4f^7 \rightarrow 4f^5 5d^{1}(5_{2/3})$ band of Eu$^{2+}$. The efficiency of UV excitation for the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ in the preform increased and we believe this resulted from the presence of Eu$^{3+}$ in the preform. Similar observations have been reported for Pb$^{2+}$ and Eu$^{3+}$ co-doped glasses [15]. These were attributed to energy transfer from the sensitizing ion Pb$^{2+}$ to Eu$^{3+}$. This leads us to believe that energy transfer from Eu$^{2+}$ to Eu$^{3+}$ was responsible for the 302 nm band, which is a new energy transfer mechanism. We have not yet determined whether the transfer is radiative or non-radiative and variation of the

Table 1

<table>
<thead>
<tr>
<th>Absorption (nm)</th>
<th>Emission (nm)</th>
</tr>
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<tr>
<td>$Eu^{3+}$</td>
<td></td>
</tr>
<tr>
<td>$4f^7 \rightarrow 4f^5 5d^{1}(5_{2/3})$</td>
<td>255</td>
</tr>
<tr>
<td>$4f^7 \rightarrow 4f^5 5d^{1}(5_{1/2})$</td>
<td>316</td>
</tr>
<tr>
<td>$Eu^{2+}$</td>
<td></td>
</tr>
<tr>
<td>Energy transfer Eu$^{2+} \rightarrow Eu^{3+}$</td>
<td>302</td>
</tr>
<tr>
<td>$^{5}D_{0} \rightarrow ^{7}F_{2}$</td>
<td>528, 539</td>
</tr>
<tr>
<td>$^{5}D_{2} \rightarrow ^{7}F_{2}$</td>
<td>574, 5</td>
</tr>
<tr>
<td>$^{5}D_{0} \rightarrow ^{7}F_{3}$</td>
<td>583, 587.5, 597</td>
</tr>
<tr>
<td>$^{5}D_{0} \rightarrow ^{7}F_{4}$</td>
<td>610, 616.5, 625</td>
</tr>
<tr>
<td>$^{5}D_{1} \rightarrow ^{7}F_{3}$</td>
<td>635.5</td>
</tr>
<tr>
<td>$^{5}D_{0} \rightarrow ^{7}F_{4}$</td>
<td>692, 702</td>
</tr>
</tbody>
</table>

Fig. 8. Emission spectra of the preform when excited at 317 nm (---, a), 405 nm (---, b), 425 nm (---, c) and 462 nm (---, d), where the emission at $\lambda > 570$ nm is due to the Eu$^{3+}$ ions and the main emission band in the 350–570 nm region is due to Eu$^{2+}$ ions.
concentration of Eu ions is being studied to determine the dominant contribution.

Emission spectra are shown in fig. 8 with excitation wavelengths at 317, 405 and 425 nm for Eu$^{2+}$ and at 462 nm for Eu$^{3+}$. As the excitation wavelength for the Eu$^{2+}$ ion increased from 317 nm to 405 and 425 nm, the peak wavelength of emission also increased. This behavior is discussed below. The assignments of the radiative transitions are summarized in table 1.

3.3. IR spectra

Vibrational spectroscopy may be used to obtain information on the effects of glass composition and different processing techniques [16]. In this study, IR absorption spectra of a preform fabricated by MCVD using an organometallic aerosol delivery technique were measured and vibrational modes were analyzed. Transparent pellets were made from mixed powder of 98 wt% KBr and 2 wt% preform core. The absorption spectra were measured using a Perkin-Elmer 1600 FT IR spectrophotometer in the infrared region between 200 and 2000 cm$^{-1}$. The spectrum is shown in fig. 9. The absorption bands of the preform centered at 465, 800, 1060, and 1150 cm$^{-1}$ were measured, consistent with the intrinsic bands of the silica tetrahedra [17].

In the fabrication process, carbon was present in the glass and additional processing, described above, was needed to eliminate it. Vibrational modes of carbon-containing compounds in such a system would occur in the infrared at, for example [18]: C–H stretching (2940–2855 cm$^{-1}$), H–C–H symmetric bending (1470 cm$^{-1}$) and asymmetric bending (1385 cm$^{-1}$), and Si–O–C bending (1100–1050 cm$^{-1}$). These bands would be sharp compared with the bands of the silica glass network, so trace amounts of carbon compounds should be detected in the IR spectra as a superposition of sharp carbon peaks on broad silica bands. No such peaks were observed and we believe carbon compounds were eliminated from the glass matrix.

For a multi-component glass, the vibrational modes of non-bridging bonds can be detected near 900 cm$^{-1}$ as a consequence of different oxygen coordination numbers for the cations [19]. In the aluminosilicate glass perform investigated here, there was only a weak band around 920 cm$^{-1}$, and aluminium ions, acting as network formers, were found to have a coordination number of four, as in the SiO$_4$ tetrahedra.

![Fig. 9. IR absorption spectrum of the core of the preform described in the text.](image-url)
Table 2
Assignment of vibrational modes

<table>
<thead>
<tr>
<th>IR bands (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>465</td>
<td>ν₁(TO) Si-O-Si bending</td>
</tr>
<tr>
<td>580</td>
<td>ν₁(Si-O-Si) defect</td>
</tr>
<tr>
<td>800</td>
<td>ν₂(TO) Si-O stretching</td>
</tr>
<tr>
<td>1060, 1130</td>
<td>ν₃(TO) Si-O stretching</td>
</tr>
<tr>
<td>1220</td>
<td>asymmetric stretch of SiO₄ unit in the chain influenced by the bonding configuration relative to Eu ion</td>
</tr>
<tr>
<td>1324</td>
<td>P-O bond stretching</td>
</tr>
</tbody>
</table>

The ligand field of rare earth ions can affect the neighboring bonding configuration of the glass network and such changes in the IR and Raman bands have been reported by Sun and Risen [20] for Pr³⁺ and Dy³⁺ ions in phosphate glasses. We noted a similar phenomenon, in that an additional band near 1220 cm⁻¹ was observed at the shoulder of a Si-O stretching band centered at 1130 cm⁻¹. This band was believed to be caused by an asymmetric stretching of SiO₄ unit influenced by the bonding configuration relative to Eu ions.

A weak band centered at 580 cm⁻¹ was observed. According to Bates et al. [21], this was due to electronic defects similar to Si E' centers represented as =Si⁺⁺⁺O⁻⁻⁻Si⁺⁺⁺. In addition to these bands, a weak band near 1324 cm⁻¹ was assigned as the P-O bond stretching mode in accordance with reported data [17]. A very weak OH vibrational mode was found near 1600 cm⁻¹. The spectral positions of the bands and their assignments are given in Table 2.

4. Discussion

A comparison of UV-photo refractivity between the same Eu-doped aluminosilicate fiber and Ge-doped fibers has been reported by Hill et al. [22]. The magnitude and spectral dispersion of the index change were reported to be nearly identical for both the Eu-doped aluminosilicate and the Ge-doped fiber for measurements made under the same experimental conditions. In Fig. 4, the strong UV absorption band near 255 nm has been assigned as the 4f⁵ → 4f⁶5d¹(1–2g) of Eu²⁺ ions and photorefractivity was observed in this band by using KrF excimer laser at 249 nm. This relation between UV absorption bands and photosensitive wavelength range has been observed in germanosilicate fibers [10], which suggested that the GeO absorption band was responsible for photorefractivity of the fibers.

In this Eu²⁺/Eu³⁺-doped fiber, there was no germanium present and only the doped ions could be related to the UV-photosensitivity. Based on similarities in the UV absorption spectra and photorefractivity between this Eu-doped fiber and Ge-doped fibers, we speculate that the photorefractivity in the Eu-doped fiber is related to the Eu²⁺ ion.

It was found that the fabrication process provided a Eu²⁺ rich environment in the fibers studied. Attempts to control the oxidation state of Eu ion by variation of the precursors have met with some success. The formation of different oxidation states for the Eu ions and their spatial distribution in the preform is not fully understood. We have also used nitrate salts in an aqueous solution instead of organometallic precursors. The nitrates were chosen to investigate the role of carbon in the organometallic soots as a reducing agent. The precursors were provided by a solution of 0.9 g Al(NO₃)₃ × 9H₂O, 0.5 g Eu(NO₃)₃ × 6H₂O and 2.0 g Aerosil 200 in 48 ml H₂O and 2 ml HNO₃. Aerosil 200 is an extremely fine SiO₂ powder with a surface area of 200 m²/g. It was dispersed in the solution using an 1.5 MHz ultrasonic bath. The HNO₃ was added to hydrolyze the surface of the powder and thus keep the viscosity low. The deposition and collapse cycle were run in a pure O₂-atmosphere in order to make an oxidizing condition to favor of Eu³⁺ ions. During the sintering cycle at up to 1900°C, we observed a weak red thermoluminescence from the peroxynitrite which was attributed to Eu²⁺. When the temperature was increased to 2100°C, the thermoluminescence started to shift towards the blue color. After the first collapse-pass at 2100°C the fluorescence had entirely the blue color of Eu²⁺. From these experimental observations, we concluded that the Eu³⁺ was less stable under the collapse conditions. The conditions under which the glass was deposited did not influence
Table 3
Comparison of $^5D_0 \rightarrow ^7F_j$ Transitions of Eu$^{3+}$

<table>
<thead>
<tr>
<th>Transitions</th>
<th>Max A (nm)</th>
<th>RA*</th>
<th>RI**</th>
<th>RI ($F_2O_3$)</th>
<th>RI ($S_iO_2$)</th>
<th>RI ($GeO_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^5D_0 \rightarrow ^7F_0$</td>
<td>574.5</td>
<td>0.71</td>
<td>1.70</td>
<td>0.036</td>
<td>0.130</td>
<td>0.110</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_1$</td>
<td>597.0</td>
<td>1.00</td>
<td>1.00</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_2$</td>
<td>616.5</td>
<td>7.91</td>
<td>9.15</td>
<td>3.000</td>
<td>4.250</td>
<td>6.666</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_3$</td>
<td>653.5</td>
<td>0.49</td>
<td>0.67</td>
<td>0.219</td>
<td>0.314</td>
<td>0.260</td>
</tr>
<tr>
<td>$^5D_0 \rightarrow ^7F_4$</td>
<td>703.0</td>
<td>0.72</td>
<td>1.03</td>
<td>1.026</td>
<td>0.398</td>
<td>0.666</td>
</tr>
</tbody>
</table>

* RA: relative area, ** RI: relative intensity.

The wavelengths are for the aluminosilicate glass preform and the data for other glasses are from the ref. [23].

This behavior. Carbon did not play any significant role as a reducing agent. This preform was phase-separated due to high concentration of dopants and detailed spectroscopic studies have not been carried out.

In fig. 7, the excitation bands of Eu$^{3+}$ in the preform showed different behavior than the Eu$^{3+}$ ions present in an alkaline silicate glass. A significant decrease in intensity of the $^7F_0 \rightarrow ^5L_6$ (392 nm) was observed in the preform compared with the alkaline silicate glass. In the preform, the excitation bands of Eu$^{3+}$ were more broadened and the doublet of $^7F_0 \rightarrow ^5D_2$ visible in the alkaline silicate was no longer resolved. In addition, the $^7F_0 \rightarrow ^5D_1$ and $^7F_1 \rightarrow ^5D_1$ transitions were not resolved clearly in the preform.

In curve d of fig. 8, emission lines for transitions from $^5D_1$ and $^5D_0$ to $^7F_0$ levels of Eu$^{3+}$ are shown. Among these transitions, only the $^5D_0 \rightarrow ^7F_1$ transition is magnetic dipole allowed with selection rules $\Delta J = 1$, and $\Delta L = 0$, $\Delta S = 0$, $\Delta l = 0$ [23]. The $^5D_0 \rightarrow ^7F_2$ emission line has been called the hypersensitive line because it is sensitive to the crystal field mixing of f and d orbitals [13]. From the emission intensity ratio between the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions, it was possible to estimate the mixing of 4f with 5d orbitals in the host material [24]. The area under the

Fig. 10. Emission spectrum of Eu$^{3+}$ ion in the preform in the 560–610 nm region. Here, curve d in fig. 8 is expanded to show fine structure in the spectrum.
$^5D_0 \rightarrow ^7F_j$ fluorescence lines represents the probability of each transition [23].

The relative intensities and areas for the $^5D_0 \rightarrow ^7F_j$ transitions for this aluminosilicate, europium-doped preform are summarized and compared with phosphate, silicate and germanate glass host [25]. In table 3, the intensity ratio ($^5D_0 \rightarrow ^7F_2$)/($^5D_0 \rightarrow ^7F_1$) was 9.15 in the aluminosilicate preform. The relative intensity of the most forbidden transition $^5D_0 \rightarrow ^7F_0$ increased by a factor of 10 in the preform when compared with the other glasses. The mixing of the 4f and 5d orbitals of Eu$^{3+}$ in the aluminosilicate preform made by MCVD with an aerosol delivery technique was found to be stronger than other single component oxide glasses made by melting. The

![Graph A](image1)

![Graph B](image2)

**Fig. 11.** Characteristics of the $4f^{5}5d^1(e_g) \rightarrow 4f^7$ emission band of Eu$^{3+}$ ions in the preform. Here the maximum of the emission band was measured for different excitations. (a) In energy scale (cm$^{-1}$), (b) in wavelength scale (nm).
glass formers of the preform, aluminum and phosphorus, replace the silicon in SiO₄ tetrahedra, thus producing a different environment for the Eu⁺² ions. These glass formers in the network may also play a role in the enhancement of crystal field mixing.

As shown in fig. 10, the splitting of 5D₀ → 7F₁ of Eu⁺³ into three lines (583, 587.5 and 597 nm) indicates the removal of the degeneracy of the 7F₁ state in the preform. This is taken to be consistent with the Eu⁺³ ions being in a distribution of C₃ sites, as observed for Eu⁺³ in other glass hosts [23]. An estimate of the number of sites in glass can be obtained by comparing the half linewidth of 5D₀ → 7F₀ transition in glasses with that in the Eu₂O₃ crystal [25]. The half width of 5D₀ → 7F₀ transition in a Eu₂O₃ crystal is 2 cm⁻¹, and in the core of preform it was 220 cm⁻¹. In comparison, the half bandwidths in germanate glass, silicate glass and phosphate glasses are given in table 3. The band for the preform glass was found to be more inhomogeneously broadened due to a wide distribution of sites, and this could explain the observed broadening of 7F₀ → 5D₂, 7F₀ → 5D₁, and 7F₁ → 5D₁ lines in the preform.

Concerning the broad Stokes shifted 4f⁵5d¹ (e_g) → 4f⁷ emission band of Eu⁺², as the excitation wavelength increased beyond a certain boundary (375 nm) near the edge of the 4f⁷ → 4f⁵5d¹(e_g) absorption band, the maximum of the emission also increased in the preform. This is shown for excitation at 317, 405 and 425 nm, for example, as curves a, b and c, respectively, in fig. 8. A linear relation between the excitation and emission was observed from a plot of many such curves and is presented in fig. 11. This behavior is similar to the reported results for Eu⁺³ in aluminosilicate bulk glass [26]. The relaxation energy, which is the difference between excitation and the energy at the maximum of the emission band, is plotted for Eu⁺² as a function of the excitation energy in fig. 12. In the figure, evidence for two different non-radiative relaxation mechanisms is observed. For the absorption bands of Eu⁺² between 27000 and 40000 cm⁻¹, the relaxation energy shows a linear dependence on excitation energy. Near the absorption edge where the linear correlation between excitation and emission started, the relaxation energy remained in the range of 2000-3000 cm⁻¹.

The excitation and emission bands of the Eu⁺² ion have been reported in binary alkali earth silicate hosts with various composition of CaO,
MgO and SiO₂ [27]. For CaO·MgO·2SiO₂, whose local structure is monoclinic, the fluorescence was centered around 430 nm. The absorption bands were near 250 and 350 nm, similar to this study. For 3CaO·MgO·2SiO₂, and 3CaO·3MgO·2SiO₂, whose structures are orthorhombic and tetragonal respectively, the emission bands shifted to 480 and 520 nm with excitation bands extended to longer wavelengths. The spectra of our aluminosilicate preform show that the Eu²⁺ ions are in a distribution of sites, and this appears to be true also for Eu³⁺. Compared with the fluorescence and excitation spectra of the Eu²⁺ ions in the 2CaO·yMgO·2SiO₂ host, in the aluminosilicate preform the majority of Eu²⁺ ions was believed to be monoclinic with a distribution of structures such as orthorhombic and tetragonal. As long as excitation energy is within the 4f⁷ → 4f⁷5d⁹(e_g) absorption band, electrons relax down to the bottom of the 4f⁷5d⁹(e_g) level of Eu²⁺ in a monoclinic host with multiphonon emission. From this energy state, the emission occurs around 420 nm regardless of the excitation energy. The relaxation energy shows a linear dependence on excitation indicating a typical Stokes shifted fluorescence with multiphonon emission. Beyond the band edge, the distribution of absorption bands of different structures become evident. Clearly, the color of the emission depends on the specific sites excited.

5. Conclusions

The UV photosensitivity of the Eu-doped aluminosilicate fiber was found to be related to the presence of Eu²⁺ ions since the photosensitive wavelength (249 nm) coincided with the 4f⁷ → 4f⁷5d⁹(e_g) absorption band of the Eu²⁺ ion. Energy transfer from the Eu²⁺ ion to the Eu³⁺ ion was observed in the UV range with an enhancement of the UV excitation for the 5D₆ → 7F₂ transition of Eu³⁺. The mixing of d and f orbitals was observed to be more effective in the preform. We observed increased inhomogeneous broadening in the preform. The linear relation between the excitation and emission of Eu²⁺ was explained by the distribution of local symmetries around Eu²⁺ ion, since they have different emission bands. The strong UV absorption associated with the Eu²⁺ and Eu³⁺ in the glass may make it possible to write index gratings holographically, and this is currently being attempted using the 337 nm emission of a nitrogen laser and that at 317 nm from a frequency doubled dye laser. The main vibrational modes associated with SiO₄ tetrahedra were measured in the preform fabricated using an aerosol modification of MCVD. The results were consistent with silicate glasses made by conventional MCVD methods.

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