Absorption and Luminescence Spectroscopy of Eu^{3+} in Lead Silicate Glasses

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Abstract

The absorption and luminescence spectra of a lead silicate glass containing Eu^{3+} as impurity have been measured. The doping ion was found to occupy two classes of non-centrosymmetric sites. The intensities of the $4f^6 \rightarrow 4f^6$ transitions are perturbed by the interaction with low-lying charge-transfer states. The quantum yield of the luminescence from the $^5D_0$ level of Eu^{3+} is unusually low, probably because of the presence of a strong ion–phonon coupling.

Introduction

It is well known that rare-earth doped glasses are of interest for laser technology [1], particularly because they are available at a low cost and are easily prepared, with respect to single crystals. So, a study of the luminescence process and of the radiative and non-radiative decay of the impurity levels is necessary to evaluate some fundamental data, such as the radiative lifetime and the luminescence quantum yield of the excited states. In fact, these parameters are important in order to estimate the threshold power for the laser excitation [2].

On the other hand, as far as the theoretical aspects are concerned, several authors have used the Eu^{3+} ion as a probe to understand the symmetry of the sites in which a rare-earth ion can be embedded in a glass [3–5]. For these reasons we investigated from this point of view the glass system PbO/SiO_2 with this kind of probe, bearing in mind that the structure of the lead silicate glasses is not completely understood [6].

The choice of this kind of host matrix is also due to the fact that it contains a high concentration of the polarizable Pb^{2+} ion. Its presence could influence the nature of the chemical bond between the rare-earth ion and its surroundings and so could affect the radiative transition probabilities and the intensity of the bands if compared with glasses containing other modifier cations [7–9]. Moreover, a high concentration of the Pb^{2+} ion in the random network of the glass could modify the ion–phonon coupling.

In this contribution we report the absorption and luminescence spectra of Eu^{3+} in a lead silicate glass and determine its radiative transition probabilities and the lifetime of the $^5D_0$ excited level. The former are discussed in the framework of the Judd–Ofelt parametrization scheme.

Experimental

The molar composition of the lead silicate glass under investigation was 37.5% PbO, 61.5% SiO_2 and 1% Eu_2O_3. Several batches were prepared by mixing appropriate quantities of SiO_2, PbO (both Carlo Erba RPE) and Eu_2O_3 (Riedel–De Haen reagent grade) in a platinum crucible and melting them at 1200 °C for 2 h in an electrically heated muffle furnace. The samples were quenched onto a stainless steel plate and annealed at 350 °C for 6 h. They were then cut and polished for the optical measurements.

Absorption spectra in the near infrared, visible and ultraviolet regions were measured using a Cary 17 spectrophotometer. The samples were held at 293 K and 80 K in a simple laboratory-built cryostat. The 80 K absorption spectrum was recorded only in the visible region. An undoped 38% PbO–62% SiO_2 glass of the same thickness was used as reference

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sample. The excitation and luminescence spectra at 293 K and 80 K (λ_{exc} = 578, 532, 526, 464, 394, 362 and 320 nm) were obtained by means of the following experimental set-up. The excitation light was obtained by using a high pressure xenon lamp (Osram XBO 150 W/1) and a 0.5-m Jarrel–Ash monochromator with a bandwidth of $\Delta\lambda = 1$ nm for the emission spectra and $\Delta\lambda = 0.6$ nm for the excitation spectra. The emitted light, taken at right angles, was analysed by means of a 0.6-m HRS$_2$ Jobin–Yvon monochromator having a bandwidth of $\Delta\lambda = 0.8$ nm. The emitted light was detected using an EMI 9558 QAM photomultiplier and was processed by a single photon counting technique. The emission spectra were recorded and processed with an Apple II E computer. They were corrected for the wavelength response of the apparatus.

The luminescence spectrum of the undoped lead silicate matrix was measured at 293 K, exciting the sample at 320 nm, and the excitation spectrum was recorded detecting the luminescence at 604 nm.

The time–decay measurements of the luminescence from the $^5D_0$ level of Eu^{3+} were performed by exciting the sample using a 8-ns pulse width of a dye-laser pumped by a N$_2$ laser at wavelengths corresponding to the absorption transitions, using the dyes Coumarin 500 and Rhodamine 6G. The decay signal was measured using an f = 200 mm Spex double monochromator, followed by a cooled S 20 photomultiplier and a Tektronix transient digitizer, summing over several pulses. The decay time was checked over every luminescence band, and in the case of the $^5D_0 \rightarrow {}^7F_2$ transition, also inside the inhomogeneous band profile.

The refractive index of the sample was found to be $n = 1.76$ by standard techniques.

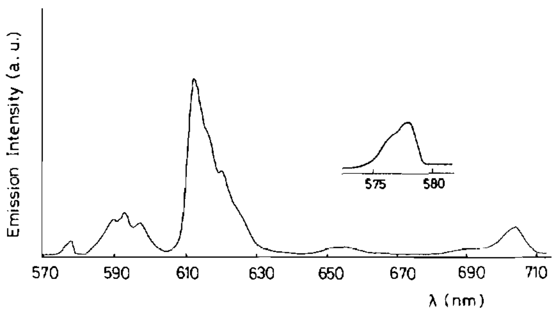

Fig. 1. Luminescence spectrum of the Eu^{3+}-doped lead silicate glass at 293 K with λ_{exc} = 464 nm. Insert: detail of the $^5D_0 \rightarrow {}^7F_0$ transition.

Results

The absorption spectra recorded at 293 K and 80 K are similar to those measured for Eu^{3+} in other systems. The assignment of the bands and the oscillator strengths, P_c (corrected for the thermal population), are reported in Table I, together with the values of the oscillator strengths obtained for the same ion in a phosphate glass [10]. It is clear that the oscillator strength of most of the transitions depends on the nature of the host matrix. We point out here that the oscillator strengths of the transitions are substantially independent of temperature.

The luminescence spectra of the Eu^{3+} ion, shown in Fig. 1, do not depend on the temperature nor on the excitation wavelengths. Analysis of the spectra suggests that the only emitting level is $^5D_0$. The assignments of the bands in these spectra, the spontaneous radiative transition probabilities and the observed branching ratios are reported in Table II.

TABLE I. Absorption Spectrum of the Eu^{3+}-doped Lead Silicate Glass at 293 K[a]

Assignment	Baricenter (nm)	P_c	
		This work	Reference 10
$^7F_0 \rightarrow {}^7F_6$	2069.2	8.61×10^{-7}	
$^7F_2 \rightarrow {}^5D_0$	610.5	2.93×10^{-7}	1.54×10^{-7}
$^7F_1 \rightarrow {}^5D_0$	586.7	2.46×10^{-8}	3.51×10^{-8}
$^7F_0 \rightarrow {}^5D_0$	577.8	8.81×10^{-9}	6.00×10^{-10}
$^7F_1 \rightarrow {}^5D_1$	532.7	2.03×10^{-7}	5.05×10^{-7}
$^7F_0 \rightarrow {}^5D_1$	525.5	2.23×10^{-8}	1.46×10^{-8}
$^7F_0 \rightarrow {}^5D_2$	464.0	3.03×10^{-7}	1.25×10^{-7}
$^7F_1, {}^7F_0 \rightarrow {}^5D_3$	411.8	shoulder	5.47×10^{-8}
$^7F_1 \rightarrow {}^5L_6$	399.8	shoulder	
$^7F_0 \rightarrow {}^5L_6$	393.3	1.11×10^{-6}	8.98×10^{-7}
$^7F_1 \rightarrow {}^5L_7$	382.8	shoulder	
$^7F_0 \rightarrow {}^5G_2, {}^7F_1 \rightarrow {}^5G_5, {}^5G_6$	378.9	shoulder	
$^7F_0 \rightarrow {}^5G_4, {}^5G_5$	375.3	shoulder	
$^7F_1 \rightarrow {}^5D_4$	364.8	shoulder	
$^7F_0 \rightarrow {}^5D_4$	362.3	3.93×10^{-7}	1.93×10^{-7}

[a]The matrix cut-off is at 340 nm.

TABLE II. Emission Spectrum of the Eu^{3+}-doped Lead Silicate Glass at 80 K

Assignment	Baricenter (nm)	Relative intensity	A (s^{-1})	Branching ratio
${}^5D_0 \rightarrow {}^7F_0$	578.0	0.089	3.8	0.015
${}^5D_0 \rightarrow {}^7F_1$	591.7	1.000	43.2	0.170
${}^5D_0 \rightarrow {}^7F_2$	609.7	3.859	166.7	0.657
${}^5D_0 \rightarrow {}^7F_3$	654.6	0.188	8.1	0.032
${}^5D_0 \rightarrow {}^7F_4$	699.6	0.733	31.7	0.125

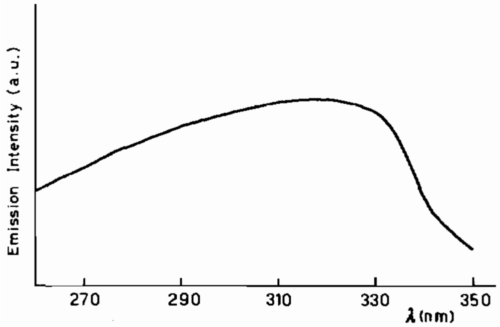

Fig. 2. Short wavelength part of the excitation spectrum of the Eu^{3+}-doped lead silicate glass at 293 K. The luminescence was detected at 612 nm.

The radiative probability of the ${}^5D_0 \rightarrow {}^7F_1$ magnetic-dipole transition was evaluated as 43.2 s^{-1} from the oscillator strength of the corresponding absorption. This figure agrees with the transition probabilities in other glasses and crystals [11]. The radiative probabilities of the other luminescence transitions were evaluated using this value as standard.

The ${}^5D_0 \rightarrow {}^7F_5$ and ${}^5D_0 \rightarrow {}^7F_6$ transitions were outside our experimental reach and could not be measured, so they were not included in the calculation of the branching ratios.

We point out that the luminescence spectrum of the Eu^{3+} ion is excited also by using wavelengths lower than 340 nm, *i.e.* inside the cut-off of the glass matrix. The excitation spectrum shows bands corresponding to the absorption spectrum of Eu^{3+} in the long wavelength part, while in the short wavelength range it shows a very broad band (Fig. 2).

In Fig. 3 we report the emission and excitation spectra of the undoped lead silicate glass matrix. The existence of a rather broad band centered at 330 nm is remarkable in this excitation spectrum.

In Fig. 4 a semilog plot of the decay time measurement of the ${}^5D_0$ level at ambient temperature is shown. The decay time for various excitation wavelengths is about 1.5 ms.

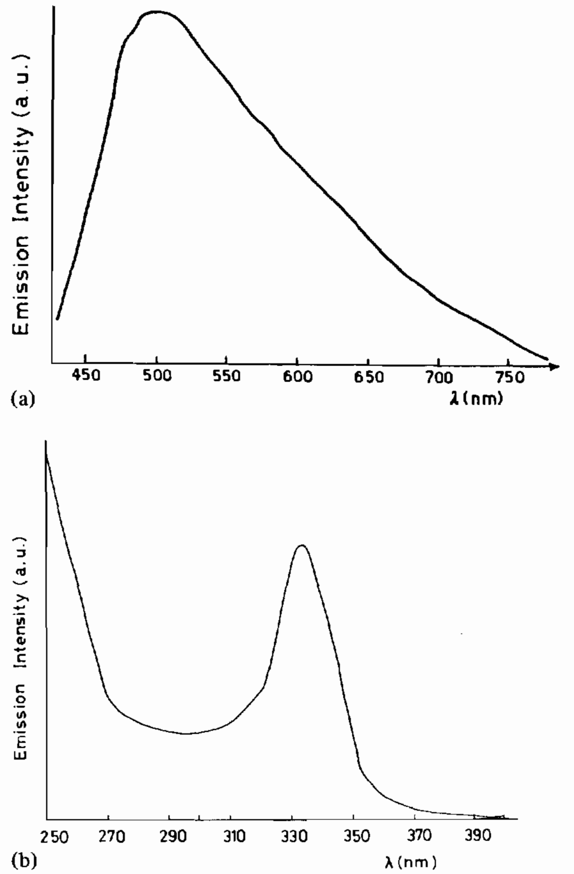

Fig. 3. (a) Luminescence spectrum of the undoped lead silicate matrix at 293 K with λ_{exc} = 320 nm. (b) Excitation spectrum of the undoped lead silicate matrix at 293 K. The luminescence was detected at 604 nm.

Discussion

(a) Site Symmetry

The bands shown in the absorption and luminescence spectra are split into several components owing to the crystal field around the Eu^{3+} ion. Only the well-resolved luminescence spectra show clearly all the crystal-field components. The luminescence bands are assigned to transitions from the nondegenerate ${}^5D_0$ level to the levels of the ${}^7F$ multiplet.

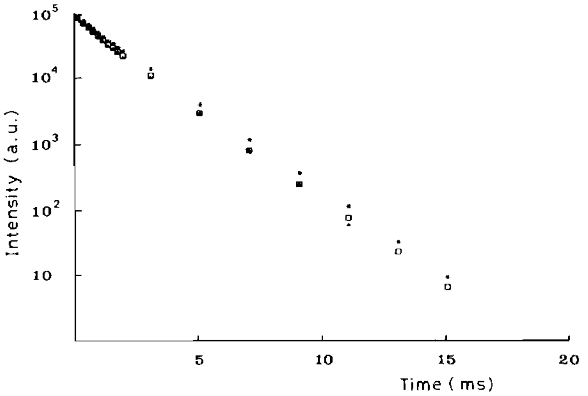

Fig. 4. Decay curve of the luminescence from the $^5D_0$ level of the Eu^{3+} ion at 293 K. *: $\lambda_{exc} = 525.5$ nm; □: $\lambda_{exc} = 532.7$ nm; ▲: $\lambda_{exc} = 577.8$ nm. The luminescence was detected at 615.0 nm.

The splitting pattern of the $^7F_1$ and $^7F_2$ levels shows that the site symmetry is so low that all degeneracy is removed. This agrees with the results of other workers concerning different glass matrices [3, 12].

The band centered at 578.0 nm, assigned to the $^5D_0 \rightarrow {}^7F_0$ transition, is clearly composed of at least two components and this can be explained only by assuming either two different classes of sites for the Eu^{3+} ion or an overlap of the nearly coincident $^5D_0 \rightarrow {}^7F_0$ and $^5D_1 \rightarrow {}^7F_3$ luminescence transitions [13]. The latter possibility can be ruled out because the spontaneous radiative transition probability calculated by means of the oscillator strength of the $^7F_0 \rightarrow {}^5D_0$ absorption transition is identical to the one determined for the 578.0 nm luminescence band. Moreover, the bandshape of the $^7F_0 \rightarrow {}^5D_0$ absorption band is clearly asymmetrical. We suggest that the Eu^{3+} ions occupy at least two classes of sites with the same geometry but with different crystal fields. In fact, it has been proposed [12] that the energy lowering of the $^7F_0$ level, and therefore the energy of the $^5D_0 \rightarrow {}^7F_0$ transition, is due to an 'avoided crossing' phenomenon between the $^7F_0$ level and the total symmetric low energy component of the $^7F_1$ one, in a holohedrized C_{2h} symmetry for a similar glass system. So the energy of the $^5D_0 \rightarrow {}^7F_0$ transition is a measure of the crystal-field strength. The difference in the crystal-field strength for the various classes of sites can thus determine the double structure of the $^5D_0 \rightarrow {}^7F_0$ transition.

The $^7F_0 \rightarrow {}^5D_0$ transition is actually strictly forbidden in the framework of the Judd–Ofelt theory. Its intensity is finite only when the A_{1p} terms are present in the crystal-field expansion [14]. For the lead silicate glass under investigation, the oscillator strength of this absorption transition is one of the highest values measured for oxide glasses ($P = 8.81 \times 10^{-9}$). The presence of the A_{1p} terms in the crystal-field expansion indicates a substantial deviation from central symmetry of the Eu^{3+} environment.

(b) Transition Intensities

The transitions responsible for the bands in the absorption and luminescence spectra can be accounted for by a magnetic-dipole or a forced electric-dipole mechanism. The intensities of the magnetic-dipole transitions are not host-dependent and are tabulated [15]; on the other hand, the intensities of the forced electric-dipole transitions can be expressed in terms of three phenomenological parameters, Ω_λ, on the basis of the Judd–Ofelt theory [7, 8]:

$$P = \frac{8\pi^2 mc\sigma}{3h(2J+1)} \frac{(n^2+2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_\lambda |U^{(\lambda)}|^2$$

$$A = \frac{64\pi^4 e^2 \sigma^3}{3h(2J'+1)} \frac{n(n^2+2)^2}{9} \sum_{\lambda=2,4,6} \Omega_\lambda |U^{(\lambda)}|^2$$

where P is the absorption oscillator strength, A is the spontaneous radiative transition probability, $(2J+1)$ and $(2J'+1)$ are the number of the states of the lower and the upper levels respectively, σ is the wavenumber and n is the refractive index. The matrix elements, $U^{(\lambda)}$, can be evaluated in the 'intermediate coupling' scheme. They have been shown to be independent of the host matrix [16]. Several sets of $U^{(\lambda)}$ have been published in the literature, but unfortunately none contains all the relevant matrix elements for the transitions we could measure in the absorption and luminescence spectra. So we were forced to use $U^{(\lambda)}$ matrix elements calculated by us [17] on the basis of the eigenstates published in ref. 18. They differ only slightly from the set kindly supplied by Prof. Jørgensen for Eu^{3+} in EuP_5O_{14}, which unfortunately did not contain the matrix elements for the $^7F_0 \rightarrow {}^5D_4$ transition.

The $4f^6$ electronic structure of the Eu^{3+} ion is such that the electronic transitions in the absorption and luminescence spectra are determined by only one Ω_λ parameter. Unfortunately, the energy level structure of the Eu^{3+} ion and the low energy cut-off of the host glass matrix allowed us to measure only three transitions determined by Ω_2, two by Ω_4 and two by Ω_6. However, as can be clearly seen in Table III, there are significant differences in the parameters calculated from the various transitions. In particular, all three Ω_λ seem to depend on the energy of the upper state involved in the transition. The neglect of J-state mixing and overlapping and poorly defined excited states such as $^5D_4$ and $^5L_6$ probably account for the differences in Ω_4 and Ω_6 derived from different transitions. The spread

TABLE III. Judd–Ofelt Parameters Ω_λ for the Eu^{3+}-doped Lead Silicate Glass

	Ω_λ (cm^2)	Baricenter (nm)
$\Omega_2(^5D_0 \rightarrow {}^7F_2)$	2.94×10^{-20}	609.7
$\Omega_2(^7F_1 \rightarrow {}^5D_1)$	7.59×10^{-20}	532.7
$\Omega_2(^7F_0 \rightarrow {}^5D_2)$	8.78×10^{-20}	464.0
$\Omega_4(^5D_0 \rightarrow {}^7F_4)$	9.85×10^{-21}	699.6
$\Omega_4(^7F_0 \rightarrow {}^5D_4)$	7.27×10^{-20}	362.3
$\Omega_6(^7F_0 \rightarrow {}^7F_6)$	6.94×10^{-21}	2069.2
$\Omega_6(^7F_0 \rightarrow {}^5L_6)$	2.18×10^{-20}	393.3

in the Ω_2 parameter is, on the contrary, still puzzling. It is possible to explain these results if there are states of opposite parity at rather low energy, so that the 'closure approximation' in the Judd–Ofelt theory cannot be used. We searched for these states by comparing the short wavelength excitation spectra of the luminescence both for the undoped and Eu^{3+}-doped lead silicate matrices shown in Fig. 2 and Fig. 3(b). The band at about 330 nm in Fig. 3(b) is certainly due to the $^1S_0 \rightarrow {}^3P_1$ transition of the Pb^{2+} ion, so the difference in the spectrum of the doped matrix can be attributed to charge-transfer transitions involving the Eu^{3+} ion. This is not surprising since Sm^{3+} shows similar behaviour [19]. Moreover, we can exclude the involvement of the $4f^5$ 5d Rydberg states of Eu^{3+} in these transitions because they occur at very high energy (68 500 cm^{-1} in CaF_2 [20]).

The mechanism responsible for the intensities can be a mixing either with charge-transfer states of opposite parity or with states of the Pb^{2+} ion, localized at about 30 300 cm^{-1}. The latter hypothesis is very appealing, but we believe it can be ruled out by the fact that Ho^{3+}-doped lead silicate glasses of the same composition show a set of Judd–Ofelt parameters very similar to the ones determined for other oxide glasses, and which are not dependent on the energy of the upper states [21]. The intensities of the forced electric-dipole transitions should then be determined by mixing with charge-transfer states, as proposed by Blasse [22] and found for germanate glasses [23].

In order to support this explanation, we evaluated the degree of covalency of the glass by determining the β nephelauxetic parameter from the energetic position of the $^1S_0 \rightarrow {}^3P_1$ transition of the Pb^{2+} ion in the glass under investigation, and comparing this value with other matrices. We found $\beta = 0.53$, which is the highest value determined for oxide glasses [10]. This parameter expresses the amount of the oxygen–rare-earth or mercury-like ion bond covalency. Its high value confirms the aforementioned interpretation.

The decay curves of the luminescence from the $^5D_0$ level proved to be substantially independent of the excitation and emission wavelengths and they are single exponential. In Fig. 4 we report such curves for different excitation wavelengths. The mean value of the lifetime is about 1.5 ms. This behaviour suggests that the different classes of sites occupied by the impurity have quite similar lifetimes, even if their crystal fields are slightly different.

The value of the lifetimes and the transition probabilities reported in Table II allow evaluation of the luminescence quantum yield, which was found to be 0.38. This value is rather low compared with the figures obtained for different glass matrices [11]. This result is quite surprising because the characteristics of the luminescence (see, for example, the transition probabilities and the branching ratios in Table II) are similar to other glass systems containing Eu^{3+}, as for instance phosphate glasses. This behaviour has no simple explanation because it is difficult to justify a stronger non-radiative relaxation by multiphonon transitions in this matrix on the basis of the phonon spectrum of the lead silicate glass. In fact, the highest vibration frequency for phosphate glasses is quoted as 1300 cm^{-1} [11], while that for lead silicate glasses is 1025 cm^{-1} [24]. This low value of the luminescence quantum yield can thus be explained only taking into account a stronger ion–phonon coupling.

As a last remark, we point out that the independence of the intensities of all the absorption and emission bands on temperature means that a static mechanism is responsible for the forced electric-dipole transitions, as was already found for the Eu^{3+} ion in a coordination compound [25].

Conclusions

In this work we measured the intensities of the absorption and luminescence transitions and the lifetime of the $^5D_0$ level of Eu^{3+} present as impurity in a lead silicate glass matrix. From these results we determined the radiative transition probabilities from $^5D_0$ to the ^7F multiplet. Moreover, we have verified that the energy levels higher than $^5D_0$ relax non-radiatively to $^5D_0$. We obtained in this way a satisfactory spectroscopic characterization of the material.

From the experimental results, it is clear that the structure of the lead silicate glass is such that the Eu^{3+} ions occupy two different classes of sites having low symmetry.

The lead silicate host matrix appears to be highly covalent and the Eu^{3+} charge-transfer states low in energy; they are involved in the mechanism which justifies the intensities of the f → f intraconfigurational transitions.

The luminescence quantum yield was found to be unusually low with respect to similar systems. The non-radiative relaxation processes appear to be highly efficient because of a strong ion–phonon coupling.

Acknowledgments

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