Optical properties of Eu^{3+}-doped fluorophosphate glasses

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Abstract. Optical absorption spectra of the Eu^{3+}-doped fluorophosphate glasses 75 NaPO$_3$–24 AF$_2$–1 EuF$_3$ (A = Mg, Ca, Ba, Zn), 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ and 58 NaPO$_3$–11 BaF$_2$–30 YF$_3$–1 EuF$_3$ have been recorded. The dipole strengths are parametrized in terms of three phenomenological Judd–Ofelt intensity parameters Ω_λ (λ = 2, 4 and 6). With the knowledge of these intensity parameters, the probability for spontaneous emission, the branching ratios and the radiative lifetime are calculated. The relation between the spectral intensities and the glass composition is discussed.

1. Introduction

In this paper, we report a spectroscopic study of trivalent europium ions in the fluorophosphate glasses 75 NaPO$_3$–24 AF$_2$–1 EuF$_3$ (A = Mg, Ca, Ba, Zn), 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ and 58 NaPO$_3$–11 BaF$_2$–30 YF$_3$–1 EuF$_3$. The aim of the study is to investigate the influence of the chemical composition on the spectral intensities in the fluorophosphate glass matrix. The spectral properties are compared with those of europium in other matrices. The trivalent europium ion is a well known spectroscopic probe [1]. Fluorophosphate glasses have been the subject of several spectroscopic investigations, due to their potential as laser host matrices [2–5]. Characteristic properties of these glasses are a low refractive index and a low dispersion [6]. The majority of these fluorophosphate glasses contain Al(PO$_3$)$_3$ or Ba(PO$_3$)$_2$ as the phosphate component. These compounds are more stable to moisture than other metaphosphates. Phosphate glasses based on the alkali metaphosphates are hygroscopic, but addition of fluorides increases the resistance to water [7]. Numerous NaPO$_3$–BaF$_2$ based fluorophosphate glasses are known, either with a high content of transition metal ions [7] or rare-earth ions [8, 9].

2. Experimental details

Sodium metaphosphate (NaPO$_3$) and CaF$_2$ were purchased from Prolabo, BaF$_2$ and MgF$_2$ from Aldrich and ZnF$_2$ from Riedel-de-Haën. Europium and yttrium fluoride were synthesized from the corresponding oxides, which were obtained from Rhône-Poulenc. The transformation of the oxide into the fluoride is done by mixing the oxide with an excess (2 × the stoichiometric amount) of ammonium bifluoride (NH$_4$F, HF) and heating

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the mixture in a vitreous carbon crucible at 300 °C for three hours. During this fluorination step a complex fluoride $(NH_4)_3LnF_6$ (Ln = Eu or Y) is formed [10]. This complex fluoride is subsequently decomposed at 450 °C. The decomposition step lasts for four hours.

The glass samples were prepared by melting the required amounts of sodium metaphosphate and the fluoride compounds in a platinum tube at a temperature of ca 900 °C. After melting, heating was continued for 15 minutes to homogenize the melt. Then, the melt was cast in a brass mould (preheated to 250–300 °C). In order to remove strain, the glass samples were annealed for four hours in an oven at 270 °C. Finally, the glass samples were cut and polished. The glasses are colourless, although under some light sources a faint pink luminescence can be observed [11]. The fluorophosphate containing ZnF_2 is slightly hygroscopic. The densities ρ of the glass samples were determined by Archimedes' method, using CCl_4 as the immersion liquid ($\rho_{CCl_4} = 1.594$ g cm^{-3} at 20 °C):

$$\rho = \rho_{CCl_4} \frac{m_0}{(m_0 - m_{CCl_4})} \tag{1}$$

where, $\rho_{CCl_4} = 1.594 - 1.9 \times 10^{-3}(T - 20)$ (T in °C), m_0 = mass of the glass sample in air (in g), m_{CCl_4} = apparent mass of the glass sample in CCl_4 (in g). The masses were determined on a semi-microbalance to the nearest 0.000 01 g. Because of the temperature dependence of the density of CCl_4, a temperature correction was necessary. Caution: CCl_4 is toxic. The error on the density measurements is estimated as being ±0.004 g cm^{-3}. The density of the glass is used for the calculation of the molar volume of the glass:

$$\bar{V} = \frac{\bar{M}}{\rho} \tag{2}$$

where $\bar{V}$ is the molar volume (in l mol^{-1}) and $\bar{M}$ is the average formula weight (in g mol^{-1}). The average formula weight $\bar{M}$ is the sum of the products of the glass components with their respective molar fraction. The reciprocal value of the molar volume multiplied by the molar fraction of the lanthanide fluoride gives the concentration of the lanthanide in the glass (in mol l^{-1}).

The refractive index n was measured on a Abbé refractometer (ATAGO 3T). A sodium lamp was used as the light source. The optical path length was measured to the nearest 0.01 cm with a micrometer. The actual composition was calculated from the exact masses of the components in the glass batch. It is assumed that the glass composition is the same as in the initial batch before melting. This assumption is reasonable because of the low volatility of the components at the processing temperature. The physical properties of the glasses used in this study are summarized in table 1.

Table 1. Optical pathlength (d), refractive index (n), density (ρ) and Eu^{3+} concentration of the glasses used in this study.

Glass	d (mm)	n	ρ (g cm^{-3})	Conc. Eu^{3+} (mol l^{-1})
75 NaPO$_3$–24 MgF$_2$–1 EuF$_3$	5.16	1.476	2.65	0.28
75 NaPO$_3$–24 CaF$_2$–1 EuF$_3$	6.48	1.484	2.65	0.31
75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$	6.80	1.495	2.79	1.35
75 NaPO$_3$–24 BaF$_2$–1 EuF$_3$	5.02	1.506	3.14	0.26
75 NaPO$_3$–24 ZnF$_2$–1 EuF$_3$	5.32	1.529	2.85	0.28
58 NaPO$_3$-11 BaF$_2$–30 YF$_3$–1 EuF$_3$	8.28	1.516	3.56	0.29

Absorption spectra were recorded at room temperature between 2500 and 300 nm with a Shimadzu UV-3100 spectrophotometer, except for the spectrum of the 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ glass at liquid nitrogen temperature, which was recorded with an AVIV 17DS spectrophotometer, equipped with an optical Dewar (Oxford Instruments). Luminescence spectra were recorded with a home-built apparatus. A water-cooled 450 W xenon lamp was used as the excitation source. Wavelength selection was achieved by a Sciencetech Model 9050 monochromator. Luminescence light was measured at an angle of 90° with respect to the excitation beam. The emission light was analysed by a McPherson monochromator (1200 lines mm^{-1}) and detected by a single-photon counting detector (photomultiplier and Stanford Research Systems SR400 two channel gated photon counter). The emission spectra are not corrected for the instrument spectral sensitivity. Wavelength calibration was done by using the emission lines of a mercury lamp. Luminescence spectra can be recorded between 350 nm and 750 nm.

3. Theoretical background

The transitions observed in the absorption spectra of trivalent lanthanide ions are intraconfigurational f–f transitions. The majority of these transitions are induced electric dipole transitions, although a few magnetic dipole transitions are known. The intensities of the transitions can be characterized by the dipole strength D:

$$D = \frac{1}{108.9 C d X_A(T)} \int \frac{A(\bar{\nu})}{\bar{\nu}} \, \mathrm{d}\bar{\nu} \tag{3}$$

where C is the concentration of the europium ion (mol l^{-1}), d is the optical path length (cm), A is the absorbance and $\bar{\nu}$ is the wavenumber (cm^{-1}). $X_A(T)$ is the fractional thermal population at temperature T (T in Kelvin) of level A from which the absorption process starts. The dipole strength is expressed in D^2 (Debye^2). According to the Judd–Ofelt theory [12, 13], the intensity of induced electric dipole transitions can be described in terms of three phenomenological intensity parameters Ω_λ ($\lambda = 2$, 4 and 6):

$$D = \frac{10^{36}}{2J+1} \frac{(n^2+2)^2}{9n} e^2 \sum_{\lambda=2,4,6} \Omega_\lambda |\langle J \| U^{(\lambda)} \| J' \rangle|^2. \tag{4}$$

The factor 10^{36} converts D^2 units into esu cm. The elementary charge e is 4.803×10^{-10} esu. The degeneracy of the ground state is equal to $2J + 1$ (i.e. 1 for Eu^{3+}). The factor $(n^2+2)^2/9n$ takes into account that the europium ion is not in a vacuum, but in a dielectric medium (n is the refractive index of the glass). Finally, the $\langle J \| U^{(\lambda)} \| J' \rangle$ are reduced matrix elements. The Ω_λ parameters can be determined by a standard least-squares fitting method. We use the reduced matrix elements reported by Carnall *et al* for the absorption spectra [14] and for the emission spectra [15].

The Judd–Ofelt intensity parameters can be used to calculate several radiative properties of the lanthanide ions. The spontaneous emission coefficient (also called probability for spontaneous emission or the Einstein coefficient for spontaneous emission) $A(\Psi J, \Psi' J')$ is given by the expression:

$$A(\Psi J, \Psi' J') = \frac{64\pi^4 \bar{\nu}^3}{3h(2J+1)} \left[\frac{n(n^2+2)^2}{9} D_{calc}^{ED} + n^3 D_{calc}^{MD} \right]. \tag{5}$$

Because an excited state ΨJ is relaxed to several lower lying states $\Psi' J'$, the radiative branching ratio β_R is defined

$$\beta_R(\Psi J, \Psi' J') = A(\Psi J, \Psi' J') \left(\sum_{\Psi' J'} A(\Psi J, \Psi' J') \right)^{-1}. \tag{6}$$

The branching ratios can be used to predict the relative intensities of all emission lines originating from a given excited state. The experimental branching ratios can be found from the relative areas of the emission lines. Once all emission probabilities that depopulate an initial level $^{2S+1}L_J$ have been calculated, they can be used to determine how fast that level is depopulated. This rate is given by the radiative lifetime $\tau_R(\Psi J)$:

$$\tau_R(\Psi J) = \left(\sum_{\Psi', J'} A(\Psi J, \Psi' J') \right)^{-1}. \tag{7}$$

Stronger emission probabilities and more transitions from a level lead to faster decay and shorter lifetimes.

4. Results and discussion

The majority of the transitions in the visible part of absorption spectrum of Eu^{3+} are very weak. The first excited free-ion level of Eu^{3+}, $^7F_1$, is only 350 cm^{-1} above the ground state $^7F_0$. At room temperature, the fractional thermal population of the $^7F_1$ level cannot be neglected: about 65% of the ions populate the $^7F_0$ level and about 35% the $^7F_1$ level. Therefore, we can observe in the absorption spectrum not only transitions starting from the $^7F_0$ level, but also from the $^7F_1$ level. The fact that these transitions often overlap makes a classical Judd–Ofelt analysis very cumbersome at room temperature. Therefore, it is advantageous to record the absorption spectrum at liquid nitrogen temperature (77 K), because at this temperature only the $^7F_0$ level is populated and as a consequence only transitions starting from the $^7F_0$ level are observed in the absorption spectrum. Because the $^7F_0$ level is non-degenerate, the approximation of the Judd–Ofelt theory that all the crystal-field levels of the ground state need to have an equal population is still valid. The intensity calculations and Ω_λ parameters for Eu^{3+} in the 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ glass can be found in table 2. An alternative approach which can be used to determine the Judd–Ofelt parameters at room temperature takes advantage of the fact that $U^{(2)}$ is the only non-zero matrix element for the $^5D_2 \leftarrow {}^7F_0$ transition and that $U^{(4)}$ and $U^{(6)}$ are the only non-zero matrix elements for the $^5D_4 \leftarrow {}^7F_0$ and $^5L_6 \leftarrow {}^7F_0$ transitions respectively. The transitions $^5D_2 \leftarrow {}^7F_0$ and $^5D_4 \leftarrow {}^7F_0$ do not overlap with the transitions $^5D_2 \leftarrow {}^7F_1$ and $^5D_4 \leftarrow {}^7F_1$ respectively. The $^5L_6 \leftarrow {}^7F_0$ overlaps partially with the $^5L_6 \leftarrow {}^7F_1$ transition, but the difference in intensity between the two transitions is so large that the contribution of the $^5L_6 \leftarrow {}^7F_1$ transition to the total dipole strength can be neglected. The three Ω_λ parameters can be determined by using the dipole strengths of these three transitions. The dipole strength of the transitions starting from the $^7F_0$ level was determined using (3) and taking a value of 0.65 for $X_A(T)$. The parameter set obtained in this way is: $\Omega_2 = 5.4 \times 10^{-20}$ cm^2, $\Omega_4 = 5.8 \times 10^{-20}$ cm^2, $\Omega_6 = 4.2 \times 10^{-20}$ cm^2. Since only three transitions are used to determine three parameters, a one-to-one agreement is found between calculated and experimental dipole strengths, and no errors could be determined on these parameters. This parameter set is comparable with the set determined by the usual fitting procedure. The Judd–Ofelt parameters for Eu^{3+} in the different glass matrices are given in table 3. Room temperature absorption spectra of the glass 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ are given in figures 1–4.
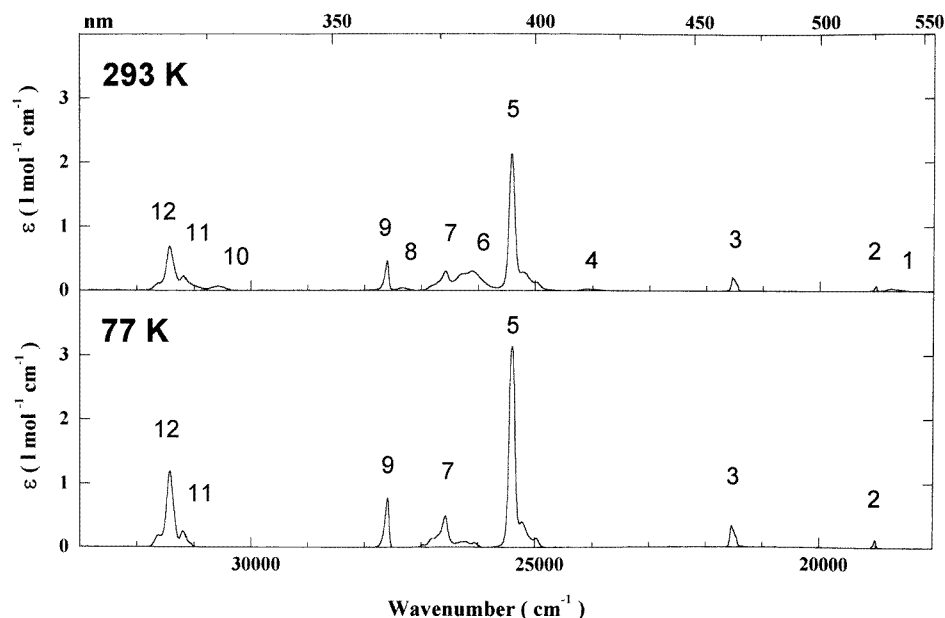
Figure 1. Absorption spectra of 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ glass at room temperature (upper spectrum) and at liquid nitrogen temperature (lower spectrum). The transitions are indicated by numbers: 1: $^5D_1 \leftarrow {}^7F_1$; 2: $^5D_1 \leftarrow {}^7F_0$; 3: $^5D_2 \leftarrow {}^7F_0$; 4: $^5D_3 \leftarrow {}^7F_1$; 5: $^5L_6 \leftarrow {}^7F_0$; 6: $^5G_{6,4,2} \leftarrow {}^7F_1$; 7: $^5G_{6,4,2} \leftarrow {}^7F_0$; 8: $^5D_4 \leftarrow {}^7F_1$; 9: $^5D_4 \leftarrow {}^7F_0$; 10: $^5H_{7,6,5} \leftarrow {}^7F_1$; 11: $^5H_4 \leftarrow {}^7F_0$; 12: $^5H_6 \leftarrow {}^7F_0$.

Table 2. Measured and calculated dipole strengths for the transitions in the absorption spectrum of the glass matrix 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ at liquid nitrogen temperature. The Judd–Ofelt parameters used for the intensity calculation are: $\Omega_2 = (5.5 \pm 1.5) \times 10^{-20}$ cm^2, $\Omega_4 = (4.2 \pm 0.9) \times 10^{-20}$ cm^2 and $\Omega_6 = (3.6 \pm 0.1) \times 10^{-20}$ cm^2. The R.M.S. value is 5×10^{-6} Debye^2.

Transition $\leftarrow {}^7F_0$	$\bar{\nu}$ (cm^{-1})	D_{exp} (10^{-6} Debye^2)	D_{calc} (10^{-6} Debye^2)	$D_{exp} - D_{calc}$ (10^{-6} Debye^2)	D_{calc}/D_{exp}
$^5D_0$	17 270	0.6	0	+0.6	0
$^5D_1$	19 010	4	3	+1	0.75
$^5D_2$	21 540	14	12	+2	0.86
$^5L_6$	25 410	173	169	+4	0.98
$^5G_2, {}^5G_4, {}^5G_6$	26 580	57	61	−4	1.07
$^5D_4$	27 590	22	15	+7	0.68
$^5H_4, {}^5H_6$	31 420	74	77	−3	1.04
$^5F_2$	32 980	12	6	+6	0.50

The hypersensitive transition $^5D_2 \leftarrow {}^7F_0$ is more intense than the magnetic dipole transition $^5D_1 \leftarrow {}^7F_0$. The ratio of the dipole strength of the $^5D_2 \leftarrow {}^7F_0$ transition to the dipole strength of the $^5D_1 \leftarrow {}^7F_0$ transition in the 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ glass is 3.5. This intensity enhancement of the $^5D_2 \leftarrow {}^7F_0$ transition with respect to the magnetic dipole transition is a general phenomenon in glasses. On the other hand, in aqueous solutions, the $^5D_2 \leftarrow {}^7F_0$ transition is less intense than the $^5D_1 \leftarrow {}^7F_0$ transition. The most intense

Table 3. Judd–Ofelt parameters Ω_λ for Eu^{3+} in fluorophosphate glasses. The intensity parameters have been determined from the absorption spectra at room temperature, except for the second set for the 75 $NaPO_3$–20 CaF_2–5 EuF_3 glass, which was determined from the spectrum at liquid nitrogen temperature (for further explanation: see text).

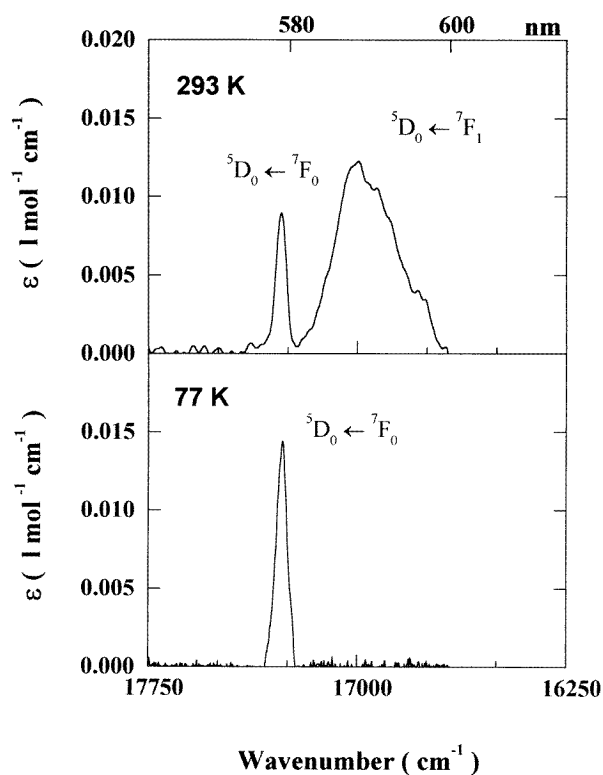| Glass	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)	Ω_6 (10^{-20} cm^2)
75 $NaPO_3$–24 MgF_2–1 EuF_3	6.5	5.4	3.9
75 $NaPO_3$–24 CaF_2–1 EuF_3	5.1	5.5	4.1
75 $NaPO_3$–20 CaF_2–5 EuF_3	5.4	5.8	4.2
	5.5 ± 1.5	4.2 ± 0.9	3.6 ± 0.1
75 $NaPO_3$–24 BaF_2–1 EuF_3	4.1	5.1	3.7
75 $NaPO_3$–24 ZnF_2–1 EuF_3	6.8	6.2	4.2
58 $NaPO_3$–11 BaF_2–30 YF_3–1 EuF_3	4.9	5.2	4.0

Figure 2. Absorption spectrum of the transitions to the $^5D_0$ state in 75 $NaPO_3$–20 CaF_2–5 EuF_3 glass at room temperature and at liquid nitrogen temperature.

transition in the UV–VIS absorption spectrum of Eu^{3+} is the $^5L_6 \leftarrow {}^7F_{0,1}$ transition, whereas the other transitions are weak to very weak.

The transitions are more intense in fluorophosphate glasses than in fluoride glasses. This is also reflected by the larger values of the Judd–Ofelt parameters for the fluorophosphate glasses. Compare for instance the Judd–Ofelt parameters in table 3 with the parameters reported for the fluorozirconate glass ZBLAN:Eu^{3+}:$\Omega_2 = 2.89 \times 10^{-20}$ cm^2, $\Omega_4 =$

Table 4. Calculated luminescence properties of Eu^{3+} in fluorophosphate glasses.

Glass matrix	Transition	A (s^{-1})	β_R	ΣA (s^{-1})	τ_R (ms)
75 NaPO$_3$–24 MgF$_2$–1 EuF$_3$	$^5D_0 \rightarrow {}^7F_6$	3.0	0.010	310	3.2
	$^7F_5$	0	0		
	$^7F_4$	74	0.236		
	$^7F_3$	0	0		
	$^7F_2$	188	0.600		
	$^7F_1$	48	0.154		
	$^7F_0$	0	0		
75 NaPO$_3$–24 CaF$_2$–1 EuF$_3$	$^5D_0 \rightarrow {}^7F_6$	3.3	0.011	290	3.5
	$^7F_5$	0	0		
	$^7F_4$	83	0.287		
	$^7F_3$	0	0		
	$^7F_2$	155	0.533		
	$^7F_1$	49	0.169		
	$^7F_0$	0	0		
75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$	$^5D_0 \rightarrow {}^7F_6$	3.4	0.011	300	3.3
	$^7F_5$	0	0		
	$^7F_4$	84	0.280		
	$^7F_3$	0	0		
	$^7F_2$	162	0.541		
	$^7F_1$	50	0.167		
	$^7F_0$	0	0		
75 NaPO$_3$–24 BaF$_2$–1 EuF$_3$	$^5D_0 \rightarrow {}^7F_6$	3.1	0.012	260	3.9
	$^7F_5$	0	0		
	$^7F_4$	75	0.292		
	$^7F_3$	0	0		
	$^7F_2$	127	0.495		
	$^7F_1$	51	0.200		
	$^7F_0$	0	0		
75 NaPO$_3$–24 ZnF$_2$–1 EuF$_3$	$^5D_0 \rightarrow {}^7F_6$	3.7	0.010	370	2.7
	$^7F_5$	0	0		
	$^7F_4$	96	0.258		
	$^7F_3$	0	0		
	$^7F_2$	219	0.588		
	$^7F_1$	54	0.144		
	$^7F_0$	0	0		
58 NaPO$_3$–11 BaF$_2$–30 YF$_3$–1 EuF$_3$	$^5D_0 \rightarrow {}^7F_6$	3.4	0.012	290	3.5
	$^7F_5$	0	0		
	$^7F_4$	78	0.271		
	$^7F_3$	0	0		
	$^7F_2$	154	0.535		
	$^7F_1$	52	0.182		
	$^7F_0$	0	0		

3.87×10^{-20} cm^2, $\Omega_6 = 2.88 \times 10^{-20}$ cm^2 [16]. An overview of intensity parameters published for Eu^{3+} systems can be found in [17]. The spectra and Judd–Ofelt intensity parameters of the fluorophosphate glasses are very comparable, so that the spectral intensities are in the first place determined by the anions (or anionic groups) around the Eu^{3+}, not by the modifying cations (Mg^{2+}, Ca^{2+}, Ba^{2+} or Zn^{2+}). The same results was found by Binnemans *et al* [18] for trivalent neodymium in fluorophosphate glasses.

The luminescence properties of the trivalent europium ion are well known. When the 75 NaPO$_3$–24 CaF$_2$–1 EuF$_3$ glass is irradiated with (ultra) violet light of 395 nm
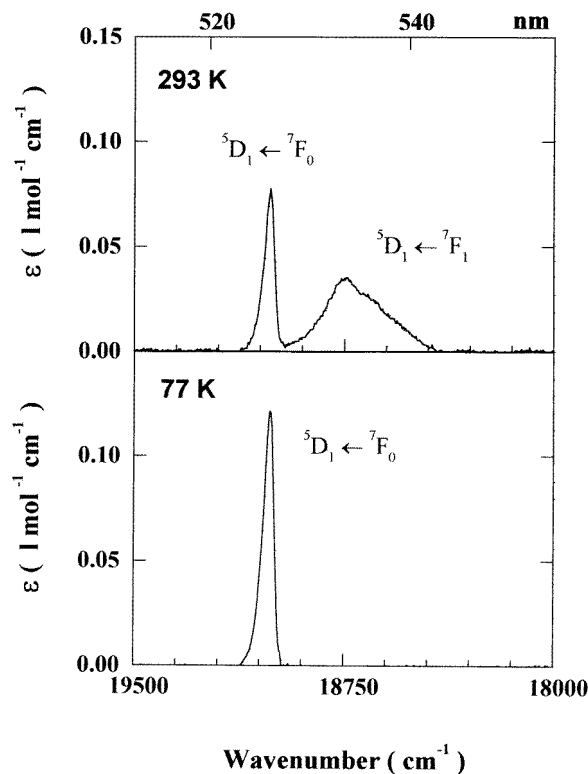
Figure 3. Absorption spectrum of the transitions to the $^5D_1$ state in 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ glass at room temperature and at liquid nitrogen temperature.

($\sim$23 500 cm^{-1}), the sample shows a very strong orange–red luminescence. The luminescence spectrum of 75 NaPO$_3$–24 CaF$_2$–1 EuF$_3$ is given in figure 5. By the irradiation, the $^5L_6$ level is populated. Even in daylight, the glass sample shows a faint pink hue, due to this luminescence. All the transitions observed in the luminescence spectrum start from the $^5D_0$ level, which is populated by radiationless deactivation of the $^5L_6$ level. The most intense transition is the hypersensitive transition $^5D_0 \rightarrow \ ^7F_2$ at 16 350 cm^{-1}. Most of the matrix elements for transitions starting from the $^5D_0$ level are zero [14], except those for the $^5D_0 \rightarrow \ ^7F_2$ transition ($U^{(2)} = 0.0032$), the $^5D_0 \rightarrow \ ^7F_4$ transition ($U^{(4)} = 0.032$) and the $^5D_0 \rightarrow \ ^7F_6$ transition ($U^{(6)} = 0.0002$). The fact that so many matrix elements are zero is due to the selection rules of the Judd–Ofelt theory. Only transitions for which $\Delta J = 2$, 4 and 6 are allowed by the induced electric dipole mechanism if luminescence starts from a level for which $J = 0$ (e.g. $^5D_0$). The $^5D_0 \rightarrow \ ^7F_1$ transition is a magnetic dipole transition. The calculated and experimental luminescence properties are summarized in tables 4 and 5. The $^5D_0 \rightarrow \ ^7F_6$ and $^5D_0 \rightarrow \ ^7F_5$ transitions could not be observed, because these are outside the measuring range of our equipment. A crystal-field splitting could be observed for the $^5D_0 \rightarrow \ ^7F_1$ transitions. The presence of three crystal-field levels indicates a total removal of the crystal-field degeneracy [19, 20]. This is an indication that the symmetry at the Eu^{3+} site is low: orthorhombic, monoclinic or triclinic. The highest possible symmetry is C$_{2v}$. Also the $^5D_0 \rightarrow \ ^7F_0$ transition is observed. The presence of this transitions cannot
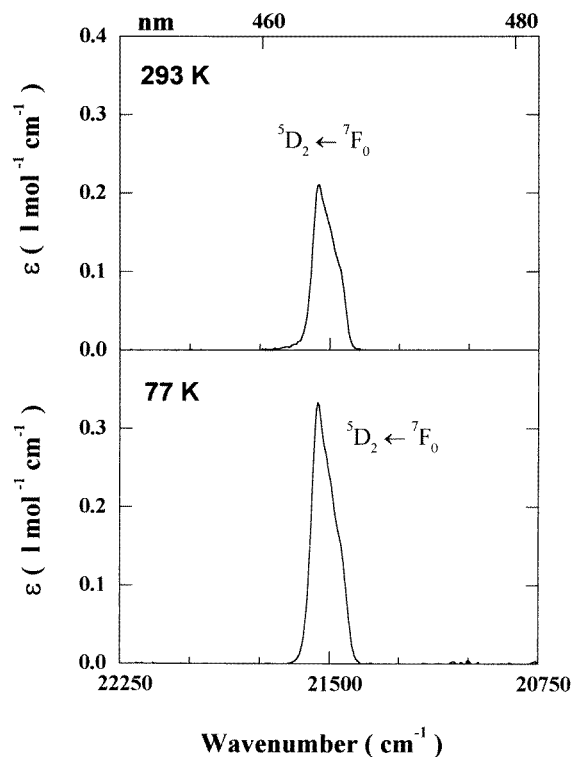
Figure 4. Absorption spectrum of the transitions to the $^5D_2$ state in 75 NaPO$_3$–20 CaF$_2$–5 EuF$_3$ glass at room temperature and at liquid nitrogen temperature.

Table 5. Transition energies, calculated branching ratios and relative intensities for the transitions observed in the luminescence spectrum of Eu^{3+} in 75 NaPO$_3$–24 CaF$_2$–1 EuF$_3$ glass.

Transition	$\bar{\nu}$ (cm^{-1})	β_R	Relative intensities
$^5D_0 \rightarrow {}^7F_6$	not observed	0.011	—
$^5D_0 \rightarrow {}^7F_5$	not observed	0	—
$^5D_0 \rightarrow {}^7F_4$	14 270	0.287	0.123
$^5D_0 \rightarrow {}^7F_3$	15 330	0	0.017
$^5D_0 \rightarrow {}^7F_2$	16 350	0.533	0.559
$^5D_0 \rightarrow {}^7F_1$	16 890	0.169	0.290
$^5D_0 \rightarrow {}^7F_0$	17 260	0	0.011

be explained within the framework of the Judd–Ofelt theory. Possible explanations for this inconsistency are discussed by several authors (for a review see [17]). The calculated radiative lifetimes of the $^5D_0$ level of Eu^{3+} in fluorophosphate glasses (3–4 ms) are larger than in oxide glasses (1–2.5 ms), but shorter than in fluoride glasses (4–5 ms).

When comparing Judd–Ofelt parameters for Eu^{3+} in different glass matrices described in the literature, one should carefully check the expression of the experimental oscillator strength or dipole strength used in these studies. Often, the fractional thermal population
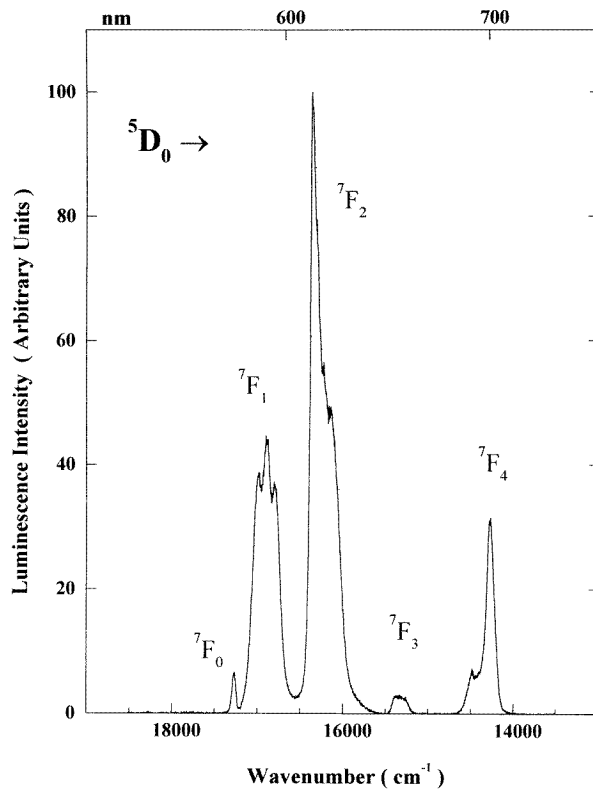
Figure 5. Luminescence spectrum of 75 NaPO$_3$–24 CaF$_2$–1 EuF$_3$ glass at liquid nitrogen temperature.

$X_A(T)$ is not taken into account. This of course influences the values of the intensity parameters. For instance, Balda *et al* [21] defined an effective oscillator strength f_{eff}. They determined intensity parameters for the fluorophosphate glass 60 NaPO$_3$–15 BaF$_2$–10 YF$_3$–15 EuF$_3$, which is comparable to our glass 58 NaPO$_3$–11 BaF$_2$–30 YF$_3$–1 EuF$_3$. Although the Judd–Ofelt parameters are quite different, both Balda *et al* and we found comparable values for the calculated radiative properties for $^5D_0$ (4.2 and 3.5 ms respectively). The experimental value for the fluorophosphate glass 60 NaPO$_3$–15 BaF$_2$–24.5 YF$_3$–0.5 EuF$_3$ is 3.8 ms [21].

5. Conclusions

This paper presents spectroscopic data of six different fluorophosphate glasses doped with the trivalent europium ion. The spectral behaviour of these glasses (spectral intensities and calculated radiative lifetimes) is intermediate between fluoride and oxide glasses. However, the spectra of the fluorophosphate glasses are very comparable, so that the spectral intensities are in the first place determined by the anions (or anionic groups) around the Eu^{3+}, not by the modifying cations. Based on the splitting of the $^7F_1$ state, it can be concluded that the symmetry of the coordination polyhedron around Eu^{3+} is C$_{2v}$ or lower.

Acknowledgments

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