

## Local structure of $\text{Eu}^{3+}$ ions in fluorophosphate laser glass

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**Abstract.** A fluorophosphate laser glass doped with 1.0 mol% of  $\text{Eu}^{3+}$  ions has been prepared and studied by site-selective spectroscopy to explore the local structure of  $\text{Eu}^{3+}$  ions. Site-selective  ${}^5D_0 \rightarrow {}^7F_{1,2}$  emission spectra have been measured under resonant excitation to the  ${}^5D_0$  level at different wavelengths within the  ${}^7F_0 \rightarrow {}^5D_0$  band at 16 K. Using the Stark level positions of the  ${}^7F_1$  and  ${}^7F_2$  levels, crystal-field analysis has been carried out. The results suggest the existence of a unique kind of site for all the environments of  $\text{Eu}^{3+}$  ions in this glass.

**Keywords.** Site-selective excitation; local structure;  $\text{Eu}^{3+}$ ; fluorophosphate glass.

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### 1. Introduction

The technique of laser-induced fluorescence line narrowing (FLN) provides a powerful tool for probing the emission properties of lanthanide (Ln) ions in glasses [1]. This technique involves the use of laser to selectively excite the Ln ions in a particular environment within an inhomogeneously broadened absorption band. The FLN technique allows one to obtain valuable information about the energy level structure, crystal-field (CF) parameters, luminescence decays, homogeneous linewidths, radiative and non-radiative transition probabilities, local coordination structure and energy transfer processes for ions in different environments in the glassy matrix [2–5]. For FLN studies,  $\text{Eu}^{3+}$  ( $4f^6$ ) ion has been proven to be the most favourite probe ion, among lanthanides, because of its simple energy-level structure at lower energies and the fact that it possesses non-degenerate ground ( ${}^7F_0$ ) and emitting ( ${}^5D_0$ ) states with well-resolved Stark components [1–3,6,7].

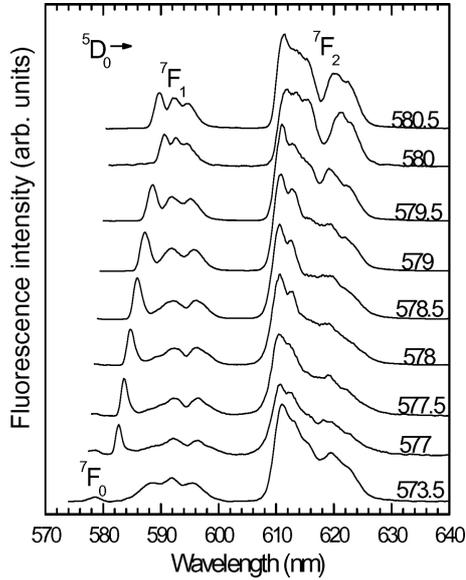
Among oxide glasses, phosphate glasses are characterized by high transparency, low refractive index, low melting temperature, good thermo-optical performance and good chemical durability [8]. Further, phosphate glasses have proven to be the most favourable host matrices for many  $\text{Ln}^{3+}$  ions because of high stimulated emission cross-sections, weak upconversion luminescence and low probability of energy-back transfer which makes them suitable for many photonic applications [9]. Fluorophosphate glasses are found attractive for laser applications and for investigating the local environment of an  $\text{Ln}^{3+}$  ion [10]. The present paper reports on the FLN studies of the  $\text{Eu}^{3+}$ -doped fluorophosphate glass. From the FLN studies, three and five Stark levels corresponding to the  ${}^7F_1$  and  ${}^7F_2$  levels have been identified and CF analysis has been carried out assuming  $C_{2v}$  orthorhombic symmetry to estimate the local structure variations in the vicinity of  $\text{Eu}^{3+}$  ions.

## 2. Experiments

$\text{Eu}^{3+}$ -doped fluorophosphate glass having the molar composition of  $55.5\text{P}_2\text{O}_5-17\text{K}_2\text{O}-11.5\text{BaO}-9\text{Al}_2\text{O}_3-6\text{BaF}_2-1\text{Eu}_2\text{O}_3$  (PKBFAEu) was prepared by melt quenching technique [8]. Refractive index was measured on Abbe refractometer at sodium wavelength (589.3 nm). The density was determined by Archimedes method. For excitation and FLN measurements, the excitation source was a dye laser operating with DCM dye, pumped by a Q-switched 532 nm frequency-doubled Nd:YAG laser. The fluorescence was dispersed by a 75 cm monochromator and observed with a Hamamatsu R928 photomultiplier tube (PMT). The signal from the PMT was fed to a digital oscilloscope and then the data were stored in a personal computer. For measurements at 16 K, the sample was cooled using a helium closed-cycle refrigerator.

## 3. Results and discussion

Figure 1 shows the FLN spectra of the  ${}^5D_0 \rightarrow {}^7F_{1,2}$  emission at 16 K obtained under resonant excitation at several wavelengths within the  ${}^7F_0 \rightarrow {}^5D_0$  inhomogeneously broadened absorption band for the PKBFAEu glass. As can be seen, due to Stark splitting, three and five distinct peaks appear for the  ${}^7F_1$  and  ${}^7F_2$  states, indicating that  $\text{Eu}^{3+}$  ions are located in sites with  $C_{2v}$  symmetry or lower. Also in the case of  ${}^5D_0 \rightarrow {}^7F_1$  emission, the high-energy component is considerably sharper than the others and its location is more sensitive to the excitation energy similar to other reported glasses [2,3,5,11]. In figure 1, the line narrowing effect is clearly visible especially for the high-energy component of  ${}^5D_0 \rightarrow {}^7F_1$  emission that shifts to lower energy linearly with the excitation wavelength. This is attributed to the progressive increase in the magnitude of local CF acting on the  $\text{Eu}^{3+}$  ions. Further, a complete loss of selectivity is observed for the emission spectrum obtained at 573.5 nm, which is at the broad maximum of the phonon absorption spectrum coupled to the  ${}^7F_0 \rightarrow {}^5D_0$  band. The spectrum is similar to the inhomogeneous one obtained with broad band excitation, which gives average  ${}^7F_1$  and  ${}^7F_2$  Stark levels due to all the  $\text{Eu}^{3+}$  ions in the PKBFAEu glass. This feature is due to the phonon side



**Figure 1.** FLN emission spectra to the  ${}^7F_1$  and  ${}^7F_2$  Stark levels exciting selectively within the  ${}^7F_0 \rightarrow {}^5D_0$  excitation band in PKBFAEu glass at 16 K. The lower spectrum is the broad-band emission to the  ${}^7F_{0,1,2}$  levels obtained by exciting the middle of the PSB (573.5 nm) coupled to the  ${}^5D_0$  level at 16 K.

band (PSB) which is common to all the  $\text{Eu}^{3+}$  ions in all the possible environments in the glass. Alternatively, it may be due to the presence of two main sites [2], energy transfer between them [5,11] or to the combination of both [11]. Though the presence of two main sites is not clear, energy migration between the  $\text{Eu}^{3+}$  ions in environments close in energy but spectrally different [11] may also be a contributing factor.

The energies of the Stark levels of the  ${}^7F_1$  and  ${}^7F_2$  multiplets were obtained from the experimental spectra by Gaussian deconvolution of the respective bands. From the Stark level positions of the  ${}^7F_1$  and  ${}^7F_2$  multiplets, CF analysis has been carried out, to know the variation of CF strength acting on the  $\text{Eu}^{3+}$  ions in the PKBFAEu glass as a function of excitation wavelength, by assuming  $C_{2v}$  site symmetry. The CF analysis was carried out using Wybourne's formalism [12]. The relevant CF parameters  $B_{kq}$  were obtained by giving the best fit between the experimental and calculated splittings of the  ${}^7F_1$  and  ${}^7F_2$  multiplets [8]. The CF parameters thus obtained are presented in table 1 as a function of excitation wavelength.

As can be seen from table 1, the CF parameters show a large variation from site to site. Out of all the parameters  $B_{22}$  presents a large variation similar to Ca diborate glass [5], while the variations of  $B_{20}$ ,  $B_{40}$  and  $B_{42}$  are about a factor of 2 and a minimum variation has been noted for  $B_{44}$  parameter. The average scalar CF strength ( $S$ ) [13] experienced by the  $\text{Eu}^{3+}$  ions is a measure of the CF interactions of  $\text{Eu}^{3+}$  ions with the surrounding oxygens and has been obtained based on these  $B_{kq}$  values. The values of  $S$ , thus obtained are given in table 1. As can be seen, the

**Table 1.** Second- and fourth-rank CF parameters (in  $\text{cm}^{-1}$ ) and CF strength parameter ( $S$ ) for different excitation wavelengths for the PKBFAEu glass at 16 K.

Exc. (nm)	$B_{20}$	$B_{22}$	$B_{40}$	$B_{42}$	$B_{44}$	$S$
577	-974	-258	1409	397	-672	437
577.5	-879	-257	1384	398	-628	415
578	-815	-273	1310	348	-671	400
578.5	-728	-303	1193	317	-670	375
579	-631	-282	1072	329	-659	363
579.5	-530	-215	929	399	-636	314
580	-471	-109	815	614	-584	307
580.5	-411	-24	635	834	-566	319

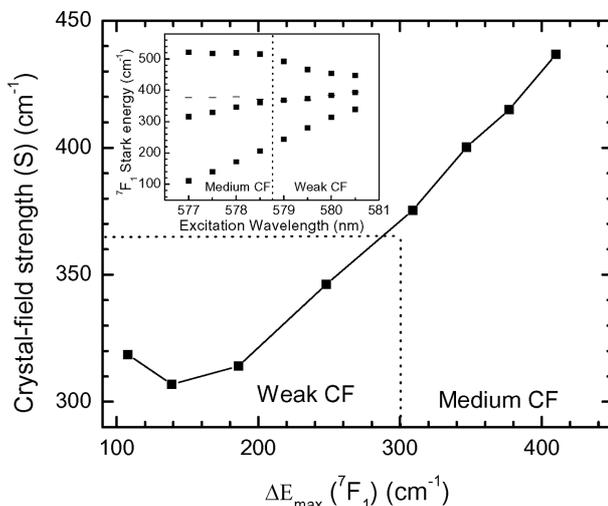
value of  $S$ , the CF strength experienced by the  $\text{Eu}^{3+}$  ions, decreases with increase in excitation wavelength.

The variation of  $S$  as a function of  ${}^7F_1$  maximum splitting ( $\Delta E_{\text{max}}$ ) is presented in figure 2. The  ${}^7F_1$  Stark level energy positions of the FLN spectra with respect to the  ${}^7F_0$  ground level are presented in the inset of figure 2 as a function of excitation wavelength. The dashed line indicates the barycentre of the  ${}^7F_1$  level. The central Stark level almost coincides with the barycentre for weak CFs whereas for medium CFs, it deviates with increase in CF strength. The high-energy Stark level deviates moderately and the deviation is large for the low-energy Stark level with increase in excitation energy. It is interesting to note that in the weak CF region, the splitting of the  ${}^7F_1$  level is almost symmetrical, with respect to the barycentre, similar to that observed in other glasses [2,5,14], whereas in the medium CF region, the barycentre shifts to higher energies with excitation energy. Based on the Gorller-Walrand and Binnemans definition [7], in the PKBFAEu glass, it is possible to make rough distribution of environments under weak [ $\Delta E({}^7F_1) < 300 \text{ cm}^{-1}$ ] and medium [ $300 \text{ cm}^{-1} < \Delta E({}^7F_1) < 450 \text{ cm}^{-1}$ ] CFs. The demarcation of weak and medium CFs is also shown in figure 2.

Variations in the distribution of environments and the CF strength parameter with the excitation wavelength show the influence of the glass composition on the local structure of  $\text{Ln}^{3+}$  ions in glasses. As the glass composition influences the optical properties and therefore the local structure of the  $\text{Eu}^{3+}$  ions, some conclusions can be made for the present glass composition. The PKBFAEu glass has larger  $S$  values and larger distribution of environments than the other  $\text{Eu}^{3+}$ -doped lead germanate [15], sodium germanate [16] and niobium tellurite [17] glasses.

#### 4. Conclusions

FLN spectra were used to investigate the variations of local environment of the  $\text{Eu}^{3+}$  ions in the PKBFAEu laser glass. The second- and fourth-rank CF parameters obtained from the Stark level positions of the  ${}^7F_1$  and  ${}^7F_2$  levels as a function



**Figure 2.** Variation of CF strength as a function of maximum splitting observed for the  ${}^7F_1$  level of the  $\text{Eu}^{3+}$  ions in the PKBFAEu glass at 16 K. The solid line is guide to the eye. The inset shows the positions of the  ${}^7F_1$  Stark levels of the  $\text{Eu}^{3+}$  ions in the PKBFAEu glass as a function of excitation wavelength. The dashed line indicates the barycentre of the  ${}^7F_1$  level.

of excitation wavelength, were used to calculate CF strength parameter. The CF strength ( $S$ ) decreases continuously with increase in excitation wavelength. The systematic variations observed in the site-selective energy positions and the presence of inhomogeneous contribution from all the  $\text{Eu}^{3+}$  ions from simultaneous excitation allow us to assume the existence of a unique site for all the environments of the  $\text{Eu}^{3+}$  ions in the PKBFAEu glass.

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