Spectral migration in ytterbium doped glasses

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Energy migration has been observed in Yb^{3+} doped Li_2O-MgO-P_2O_5 phosphate glasses. Two compositions have been investigated, with low and high modifier content. In both samples, a dipole-dipole mechanism has been found to describe the energy transfer process underlying the spectral migration. However a large difference in the average transfer rate is observed between the samples. The low migration in the sample with high modifier content is attributed to a trapping of excitation inside clusters.

Introduction

Rare earth (RE) doped phosphate glasses have attracted considerable interest in photonics applications, like waveguide lasers and amplifiers. To design efficient and highly doped active glasses, RE clustering, which induces non radiative deexcitations, has to be reduced. Among other processes related to inter-ionic separation, low temperature spectral migration is of great interest[1]. This method is based on the observation of the energy diffusion, by the measuring of the time-resolved luminescence spectra, after selective excitation inside an inhomogeneously broadened absorption band. In this paper, two glass compositions with different cluster content are investigated. Spectral migration parameters (rate, multipolarity) are determined and discussed in correlation with previous results on cooperative luminescence[2,3].

Experiment

In this study, phosphate glasses with the general molar composition $x(Li_2O\text{-}MgO)\text{-}yP_2O_5$, doped with 2 % wt. Yb_2O_3 ($\approx 1.48 \times 10^{20}$ cm^{-3}) have been investigated. The glass modifier to glass former ratio R=x/y was either 0.5 or 1.2. Details of the synthesis are described elsewhere[3]. Spectroscopic measurements were carried out at 12 K using a Helix close-cycled He cryostat. Excitation pulses (8 ns) were provided by a Ti-Sa laser (BMI TS 802). Fluorescence was detected by an InAs photodiode, with a time constant around 1µs, through a Jobin-Yvon HD 640 spectrometer. Time-resolved spectra were recorded by a computer interfaced digital oscilloscope Tektronix TDS 350.

Results and Discussion

Yb^{3+} has 13 4f-electrons and therefore only two multiplets in this configuration, $^2F_{7/2}$ (ground state) and $^2F_{5/2}$, which are separated by ≈ 10000 cm^{-1}. In glasses at low temperatures, $^2F_{7/2} \leftrightarrow {}^2F_{5/2}$ transitions are mainly inhomogeneously broadened due to site to site environment variations. Energy migration between different sites has been observed, by monitoring the time evolution of the $^2F_{5/2}(0) \rightarrow {}^2F_{7/2}(0)$ emission spectrum, after selective excitations inside the same transition. Fig.1a and b show the emission spectra of both R=1.2 and R=0.5 samples recorded after short pulse excitation at $\lambda_{exc} \approx 974$ nm and 972.9 nm, respectively, for increasing delays. In both cases, two components are clearly identified: a narrow peak with spectral width ≈ 20 cm^{-1}, corresponding to the emission from ions directly excited by the laser (resonant fluorescence), and a broad band with spectral width ≈ 60 cm^{-1}, due to the emission from ions excited through an energy transfer process (background fluorescence). The excitation wavelengths were chosen to get the same energy difference between the excitation wavelength and the broad band in both samples.

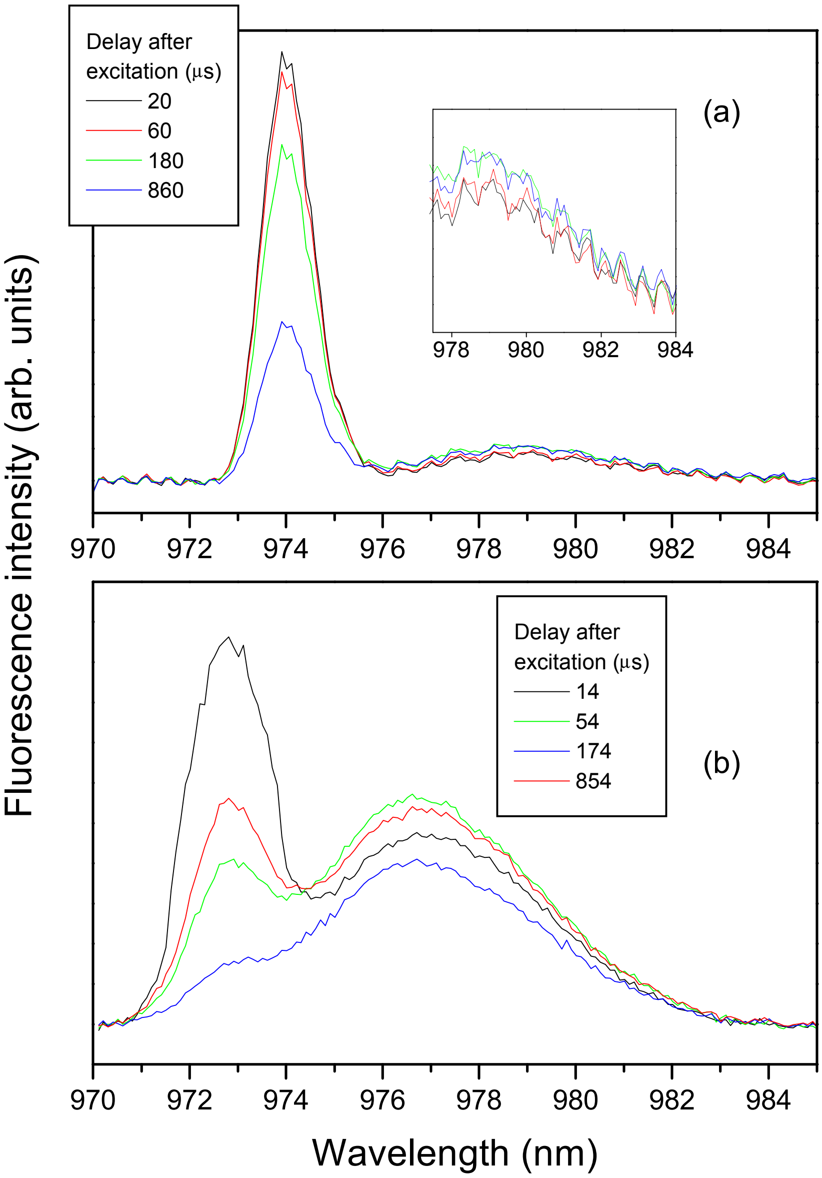

Fig. 1 :$^2F_{5/2}(0)$-$^2F_{7/2}(0)$ emission spectra recorded at increasing delays after selective excitation. (a) R=1.2, λ_{exc}=974 nm; (b) R=0.5, λ_{exc}=972.9 nm.

Concerning the migration process, two main differences for the two compositions are observed: 1) the background intensity relative to the resonant intensity is much lower for the R=1.2 sample than for the R=0.5 sample, and 2) the decay of the resonant peak is also slower for the R=1.2 sample than for the R=0.5 sample.

In order to get a more quantitative description, the narrow and broad components have been deconvoluted, and their intensities I_N and I_B integrated. At low temperature, i.e. kT much lower than the inhomogeneous broadening, an irreversible transfer model can be used. In this model, excitation can only migrate to sites with lower energy, since nonresonant transfers involving creation of vibrations are more probable. In this case, and assuming no dispersion of the radiative de-excitation rates, I_N and I_B are related by:[1]

$$I_B/I_N = \exp(\gamma\, t^{3/s}) - 1$$

where s is the multipolarity of the energy transfer mechanism and γ is a macroscopic parameter reflecting the average rate of transfer. Plots of $\ln(I_N/I_B+1)$ as a function of $t^{1/2}$ (corresponding to a dipole-dipole process, s=6), for different excitation wavelengths are presented in Fig. 2 and 3 for R=1.2 and R=0.5 samples, respectively.

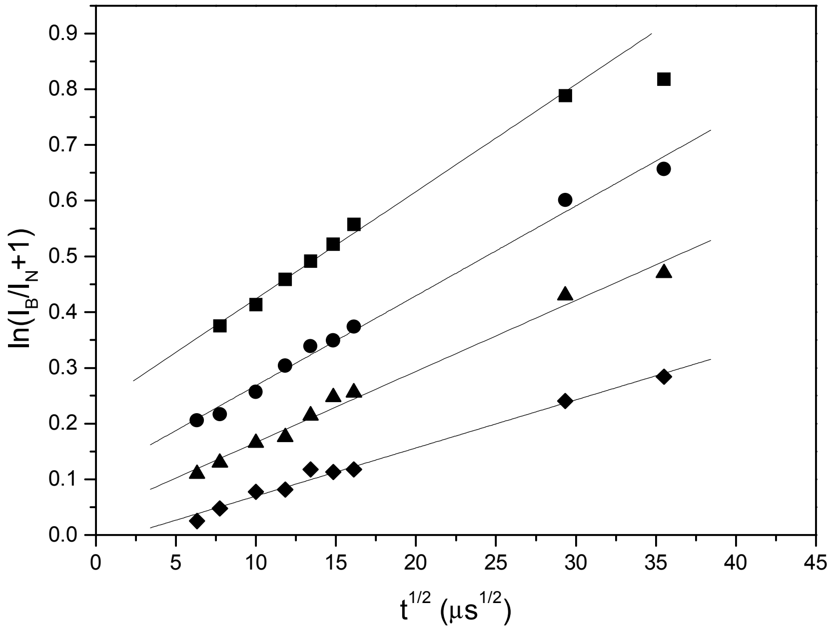

Fig. 2 : Time evolution of the ratio between the narrow and the broad components in the R=1.2 sample. Squares: λ_{exc}=973.6 nm, circles: λ_{exc}=974 nm, triangles: λ_{exc}=975.6 nm, diamonds: λ_{exc}=977.7 nm.

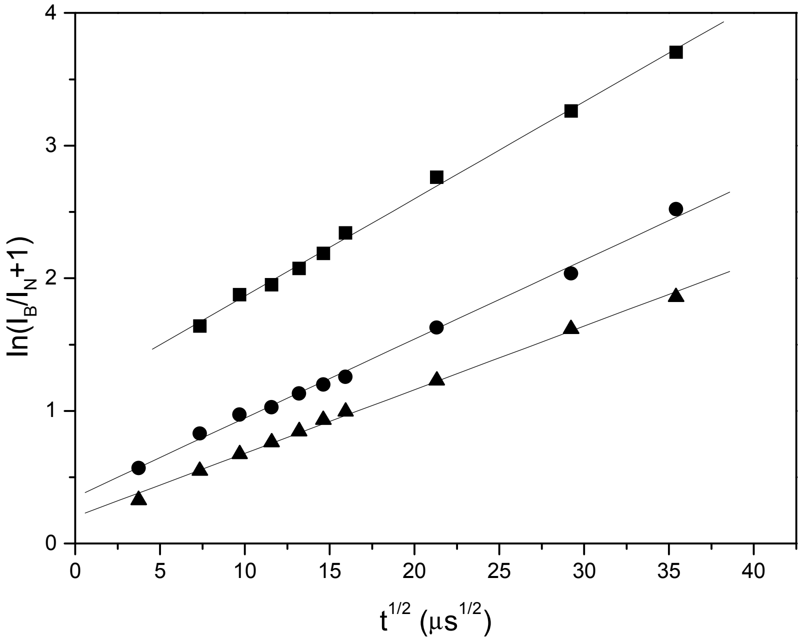

Fig. 3 : Time evolution of the ratio between the narrow and the broad components in the R=0.5 sample. Squares: λ_{exc}=972.9 nm, circles: λ_{exc}=974.1 nm, triangles: λ_{exc}=976.1 nm.

In both samples the dipole-dipole mechanism gives a satisfactory description of the migration process in its initial part. When delays are longer than about 1.2 ms, it becomes difficult to obtain reliable deconvolutions of the spectra, so that the time dependence in this region is not clearly established. On the other hand, measurements at times shortest than 15 μs must be disregarded since the narrow peak is not completely free from the laser excitation. The slopes of the fits depicted in Fig. 2 and 3 yield different values for the γ parameter, increasing with decreasing excitation wavelength. This result is not surprising, since the energy migration rate depends on the number of available sites in the energy transfer process, that is dependent on the energy excitation. This behavior is clearly shown in Fig. 4, where the migration rate γ is plotted versus the energy difference between the excitation beam and the broadband peak. These values are of the same order of magnitude as those found in other Yb^{3+} doped phosphate glasses[1]. As expected from the qualitative description of Fig.1, a large difference between the average transfer rates of the R=1.2 and R=0.5 samples is observed, with a γ value about four times higher for the R =0.5 sample. Previous cooperative luminescence intensity measurements[2,3] showed that an increase of the modifier content in these phosphate glasses, i.e. high R values, increases Yb^{3+} clustering, and therefore the interactions between neighboring ions. On the other hand, this work shows that spectral migration is greatly reduced in the sample with the highest R value, which can be explained by small energy differences among close lying ions leading to a quasi resonant energy transfer. As a result, the energy is trapped inside the clusters and migration is greatly reduced.

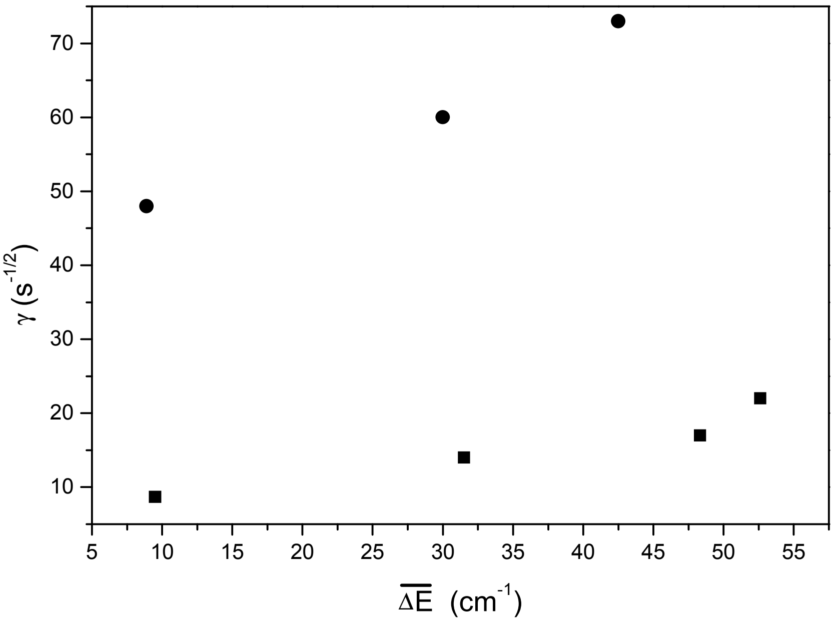

Fig. 4 : γ as a function of the average energy difference between excitation and emission. Circles: R=0.5, squares: R=1.2.

Conclusion

Low temperature spectral migration has been observed in two phosphate glasses doped with 2% wt. Yb_2O_3. After selective excitation inside the $^2F_{7/2}(0)$-$^2F_{5/2}(0)$ transition, a narrow peak and a broad band are observed in the emission spectra, which are associated with ions directly excited by the laser and through energy transfer, respectively. In both samples, the time evolution of the emission can be well fitted using a dipole-dipole process for the microscopic energy transfer between Yb^{3+} ions. However, the sample with the highest modifier content exhibits a much smaller migration rate than the one with a lower modifier content. Since the former sample contains a higher cluster concentration, this result is explained by the excitation trapping inside the clusters by a quasi-resonant energy transfer among close lying ions.

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[2] P. Goldner, B. Schaudel, M. Prassas and F. Auzel, J. Lumin. **688-690**, p. 87 (2000).

[3] B. Schaudel, P. Goldner, M. Prassas and F. Auzel, J. Alloys Compd. **300-301**, p. 443-449 (2000).