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# Cooperative luminescence as a probe of clustering in $Yb^{3+}$ doped glasses

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## Abstract

An emission centred around 500 nm under near infrared excitation has been observed in $Yb^{3+}$ doped borosilicate, aluminosilicate and phosphate glasses. Lifetime measurements and convolution of infrared luminescence spectra confirm the cooperative nature of this visible emission. Cooperative luminescence intensity, i.e. rare earth clustering, strongly depends on the glass composition studied. In the phosphate glasses, a good correlation is found between the structural evolution of the glass and the cooperative emission intensity.

*Keywords:* Amorphous materials; Luminescence

## 1. Introduction

Since the first observation by Nakazawa and Shionoya in $YbPO_4$ [1], cooperative luminescence of ytterbium ions has been reported in several hosts, mainly in crystals [2–6] except one study relating measurements in an ytterbium doped silica fibre [7]. This luminescence corresponds to the simultaneous de-excitation of two $Yb^{3+}$ ions resulting in the emission of one short-wavelength visible photon. This process relies on Coulombian interaction between ions and has a strong dependence on inter-ionic distances. Because this emission has a very low efficiency, it is favoured for nearest $Yb^{3+}$ ions, so cooperative luminescence has been proposed as a signature of rare earth ion clustering in glasses [4].

Compact-size, high-gain rare earth (RE) doped planar and fibre optical amplifiers require large activator concentrations but the formation of RE clusters is then enhanced. The gain of these devices is limited by fast energy transfers and non-radiative de-excitation which take place inside RE clusters [8,9]. In order to preserve good performances, it is necessary to limit the clustering of RE ions. Chemical composition is known to be an important parameter in the formation of clusters [10]. Cooperative luminescence measurements of $Yb^{3+}$ ions is an attractive method to characterise the tendency of $Yb^{3+}$ ions to form clusters. First, bulk materials can be directly analysed whereas usual techniques, like unsaturable absorption experiments, must be performed on fibres. The large energy gap (around 10 000 $cm^{-1}$) between $Yb^{3+}$ ground and metastable multiplets also reduces non-radiative de-excitations (multiphonon relaxation, quenching due to OH groups) compared to $Er^{3+}$ ions. Indeed, the major problem of studies concerning erbium clustering in fibres is that the quenching really due to clusters is difficult to separate from other phenomena. Here, the observed cooperative luminescence of ytterbium ions is directly due to $Yb^{3+}$ clusters and this method allows one to optimise the materials composition in order to prevent clustering.

Cooperative luminescence has been recorded in $Yb^{3+}$ doped aluminosilicate, borosilicate and phosphate glasses. First, to confirm the nature of the visible emission observed around 500 nm, properties of cooperative luminescence have been established in aluminosilicate glasses from measurements of the infrared luminescence and lifetimes of the infrared and cooperative emissions. The visible luminescence of impurities as erbium or thulium ions is also analysed because energy transfers, like Addition de Photons par Transfert d'Energie (APTE) between $Yb^{3+}$ and $Er^{3+}$ or $Yb^{3+}$ and $Tm^{3+}$, are very efficient and could hide cooperative luminescence in some cases. Finally, examples of evolution of the luminescence intensity with the chemical composition are reported and analysed by taking into account the glass structure.

## 2. Experiment

All samples were batch melt glasses. Ytterbium doped aluminosilicate and borosilicate glasses were prepared for

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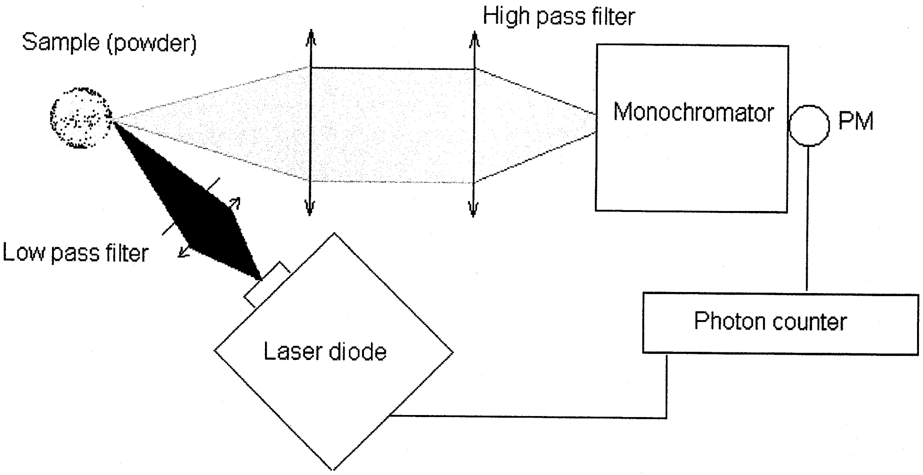

Fig. 1. Experimental setup for the measurements of the cooperative luminescence.

this study by Corning S.A. For phosphate glasses, the starting materials were melted in a furnace at 1350°C. The samples were annealed at 350°C during 2 h. The starting mixtures correspond to the compositions $x(Li_2O–MgO)–yP_2O_5$, with $R=x/y$ ranging from 0.5 to 1.5. In all the samples, the $Yb_2O_3$ concentration is 5 wt% (about $3.7*10^{20}$ $Yb^{3+}$ ions/$cm^3$, depending on the chemical composition).

To ensure good reproducibility of cooperative luminescence measurements, an experimental setup with a fixed geometry was chosen (Fig. 1). Moreover, calibrated powders (80 μm) were used and excited at 975 nm with a high power (400 mW) stable laser diode (Coherent S-98-1000C-100-Q). The fluorescence is detected using a Hamamatsu H6240-01 photon counting head connected to a Stanford Research SR400 photon counter. Fluorescence lifetimes and infrared luminescence spectra were recorded using a pulsed Ti:sapphire laser (TS802 BMI) and a $N_2$ cooled InAs detector (Hamamatsu P838).

## 3. Spectroscopic properties of $Yb^{3+}$ doped aluminosilicate glasses

The infrared emission of an 5 wt% $Yb^{3+}$ doped aluminosilicate glass, corresponding to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition, is presented in Fig. 2. Three peaks are observed at 975, 1025 and 1065 nm and are assigned to transitions

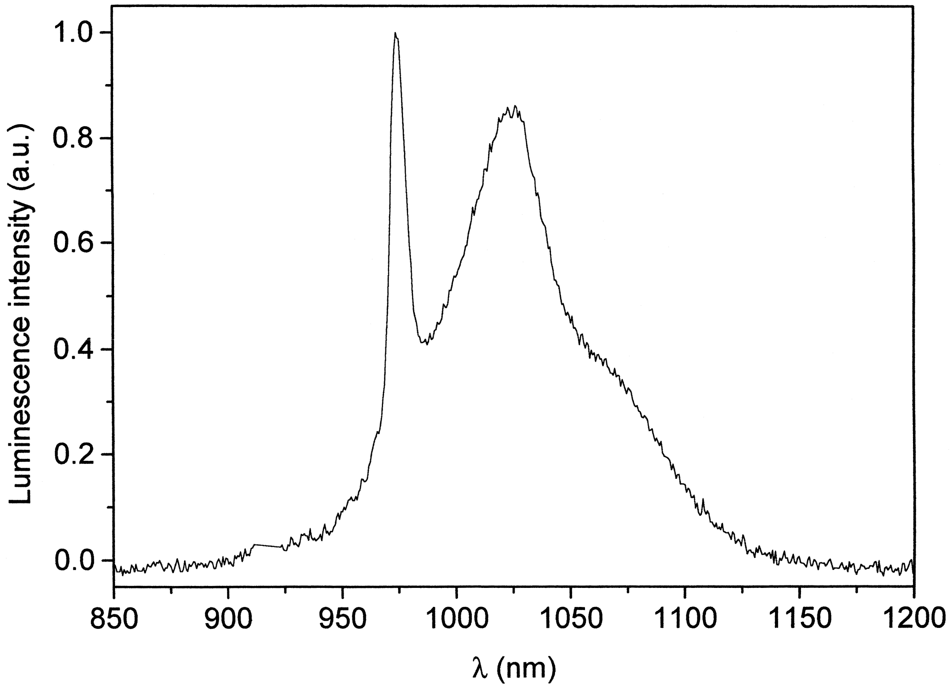

Fig. 2. Infrared luminescence spectrum of the $Yb^{3+}$ doped aluminosilicate glass.

from the first level of the excited multiplet to the ground state multiplet. The luminescence decay of the $^2F_{5/2}$ manifold is exponential with a time constant of 990 μs. This decay can be considered as completely radiative since the $^2F_{5/2}$ lifetime does not vary significantly with $Yb^{3+}$ concentration (from 0.5 wt% up to 10 wt%) and the phonon cut-off frequency of this glass is around 1100 $cm^{-1}$.

A broad and weak visible emission is also observed around 500 nm under infrared excitation (Fig. 3). To confirm the nature of this luminescence, we have first compared it with the convolution of the infrared emission spectrum.

Since cooperative luminescence results from the simultaneous de-excitation of two $Yb^{3+}$ ions, theoretical cooperative emission spectrum can be calculated taking into account all energetic combinations between Stark levels of the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds. The cooperative luminescence spectrum F(E) is then related to the infrared one $f(E)$ by:

$$f(E) = \int f(E)f(E - E')\,\mathrm{d}E'$$

Experimentally, good agreement is obtained between the convolution of the infrared emission spectrum and the cooperative luminescence spectrum (Fig. 3) although a slight discrepancy in relative luminescence intensities can be noticed. This is not surprising since the cooperative luminescence rate is not exactly equal to the square of the infrared emission rate [6,11].

A relation between the decay times of the infrared emission ($\tau_2$) and the cooperative luminescence ($\tau_{\mathrm{coop}}$) can also be obtained assuming a rate equation model. The rate equation for the energy levels of $Yb^{3+}$ has the following form:

$$\frac{\mathrm{d}N_2(t)}{\mathrm{d}t} = PN_1(t) - \frac{N_2(t)}{\tau_2} - XN_2(t)^2$$

and where $N_1$ and $N_2$ are the population densities of the ground-state and the excited-state levels, $P$ the pump rate, $X$ the cooperative luminescence rate constant. Since the infrared emission intensity $I_{\mathrm{IR}}$ is proportional to the population of excited ions $N_2$ and the cooperative luminescence is very weak, decays of the infrared and cooperative luminescence intensities can be respectively expressed as:

$$I_{\mathrm{IR}}(t) \propto N_2(t) \propto \exp\left(\frac{-t}{\tau_2}\right) \quad \text{and}$$

$$I_{\mathrm{coop}}(t) \propto N_2(t)^2 \propto \exp\left(\frac{-t}{\tau_2/2}\right)$$

The cooperative luminescence decay was recorded at 500 nm and is shown in Fig. 4. It reveals no rise time and can be fitted with a single exponential function resulting in a decay time of 450 μs. This result is consistent with the value found for the infrared emission decay time and the relations given above.

Previous results have confirmed the nature of the visible emission recorded under infrared excitation. However, other rare earth ions, involved as impurities in the doped glasses, could exhibit emissions which would add to the cooperative luminescence of $Yb^{3+}$ ions. To examine this possibility, luminescence in the range 400–600 nm has

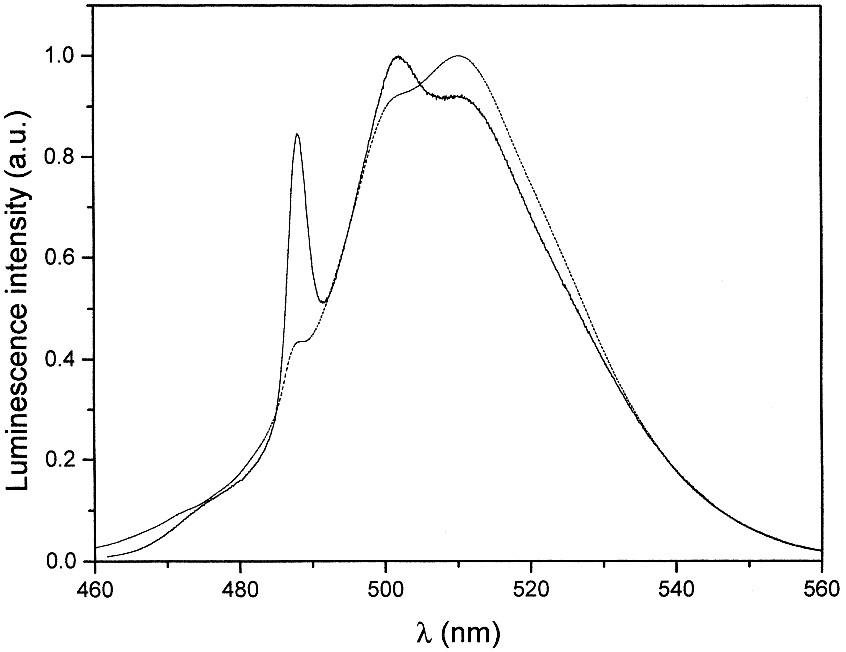

Fig. 3. Cooperative luminescence spectrum (straight line) and the convolution of the infrared luminescence spectrum (dotted line) of the $Yb^{3+}$ doped aluminosilicate glass.

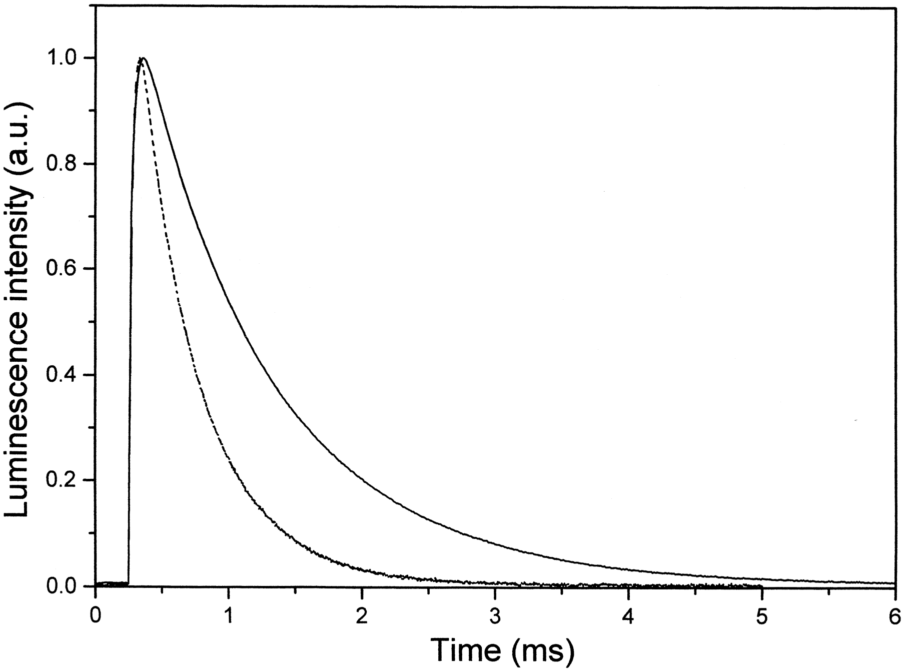

Fig. 4. Fluorescence decay curves for the cooperative (dotted line) and infrared (straight line) luminescence.

been analysed for $Yb^{3+}$–$Er^{3+}$ and $Yb^{3+}$–$Tm^{3+}$ co-doped glasses. These ions are tested because they are known to emit visible luminescence around 500 nm due to energy transfers from $Yb^{3+}$ ions and are common impurities in ytterbium oxide. We can observe in Fig. 5 that the cooperative emission of $Yb^{3+}$ ions is well separated from the luminescence of $Er^{3+}$ or $Tm^{3+}$ in silicate glasses. However, the weak emission around 475 nm in $Yb^{3+}$ doped glass is due to the presence of a few ppm of $Tm^{3+}$ ions. This is confirmed by the rise time observed on the fluorescence decay at 475 nm, which can be explained by the three successive energy transfers from $Yb^{3+}$ to $Tm^{3+}$ necessary to populate the $^1G_4$ level (inset on the left in Fig. 5). APTE transfers are very efficient, much more than cooperative effects, so the luminescence of a few ppm of impurities may be more intense than the cooperative

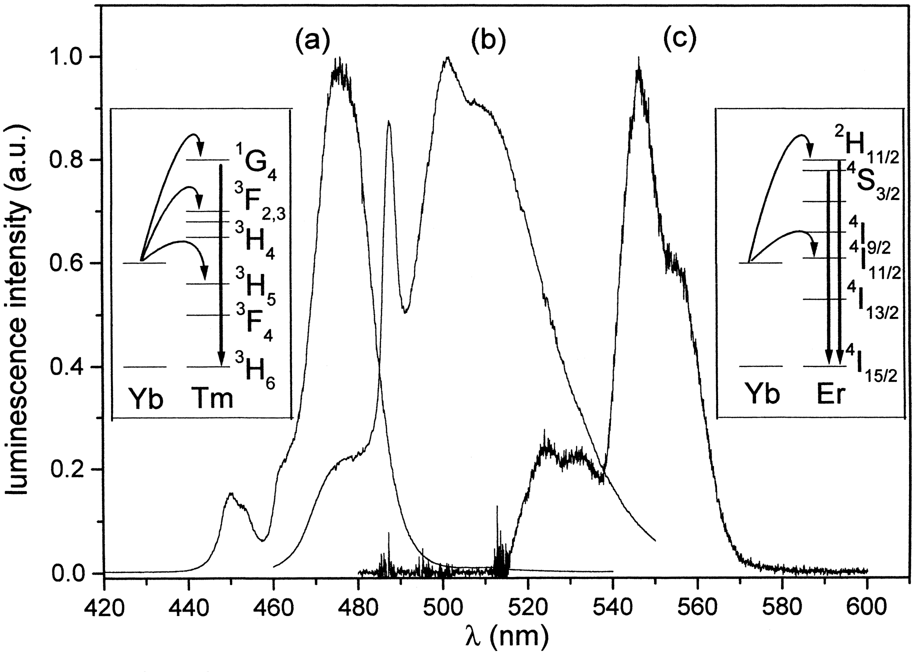

Fig. 5. (a) Visible luminescence of an $Yb^{3+}$–$Tm^{3+}$ co-doped glass due to APTE (scheme in the inset on the left), (b) Cooperative luminescence of an $Yb^{3+}$ aluminosilicate glass, (c) Visible luminescence of an $Yb^{3+}$–$Er^{3+}$ co-doped glass due to APTE (scheme in the inset on the right).

luminescence. The pollution is principally due to the starting oxide $Yb_2O_3$, ICP chemical analysis of $Yb_2O_3$ shows the presence of 10 ppm of $Tm_2O_3$ and 3 ppm of $Er_2O_3$. These small quantities are sufficient to observe visible luminescence. In order to obtain reliable results on cooperative luminescence, high purity raw materials are required for $Yb^{3+}$ doped glass synthesis.

The same study has been performed on borosilicate and phosphate glasses and has confirmed in both cases that the emission centred at 500 nm corresponds to a cooperative effect.

## 4. Dependence of cooperative luminescence intensity on chemical composition

In order to study the influence of the chemical composition on RE clustering, several compositions were synthesised in the three kinds of glasses. The aptitude of each composition to the formation of RE clusters is compared by normalising the luminescence intensities with respect to the absorbed pump power and the lifetime of the $^2F_{5/2}$ level of each sample. With these corrections, intensities can be directly compared.

Cooperative luminescence intensity for two different aluminosilicate compositions is reported in Fig. 6. A large variation of the signal is observed indicating that clustering is very dependent on the environment of the rare earth in the glass; even slight modifications in the chemical composition can induce various behaviour of the $Yb^{3+}$ ions. In borosilicate glasses (Fig. 7), the cooperative intensity is also dependent on the composition but the variations observed are less pronounced than in aluminosilicate glasses: the clustering level is reduced in borosilicate glasses. The analysis of the cooperative luminescence permits to choose chemical compositions in which the clustering is limited.

In phosphate glasses, the evolution of the cooperative luminescence has been studied as a function of the ratio $R=M_2O/P_2O_5$ (here $M_2O=Li_2O+MgO$). In Fig. 8, the cooperative luminescence intensity measured at 510 nm (to avoid a possible luminescence of $Tm^{3+}$ ions) is plotted versus R. The luminescence intensity, i.e. clustering, increases with the proportion of modifier components in the composition. This can be understood by taking into account the structural modifications in the glass when R increases [12]. For $R=0$, the glass structure is only composed of branching units ($PO_4^{3-}$ tetrahedra with three bonding oxygen atoms per phosphorus atom) and the network is three-dimensional. When R increases, middle units (with two bonding oxygen atoms per P) appear and create chains in addition to the 3D network. This is a depolymerization process and at the metaphosphate composition ($R=1$), there are nearly only middle units and therefore long chains. For R ranging between 1 and 2, end groups (with only one bonding oxygen atom per P) can form and the network becomes more and more flexible. At $R=2$, there are only pyrophosphate units (two end groups linked together). For greater R, the network is mainly composed of isolated $PO_4$ groups (orthophosphate units). When the network is mainly based on branching and middle units ($R=0.5$), cooperative luminescence is weak, indicating that the ytterbium ions are well dispersed in the glass. As R increases, the $Yb^{3+}$ ions tend to form clusters because the glass network is more flexible and the long phosphate chains do not permit to isolate efficiently RE

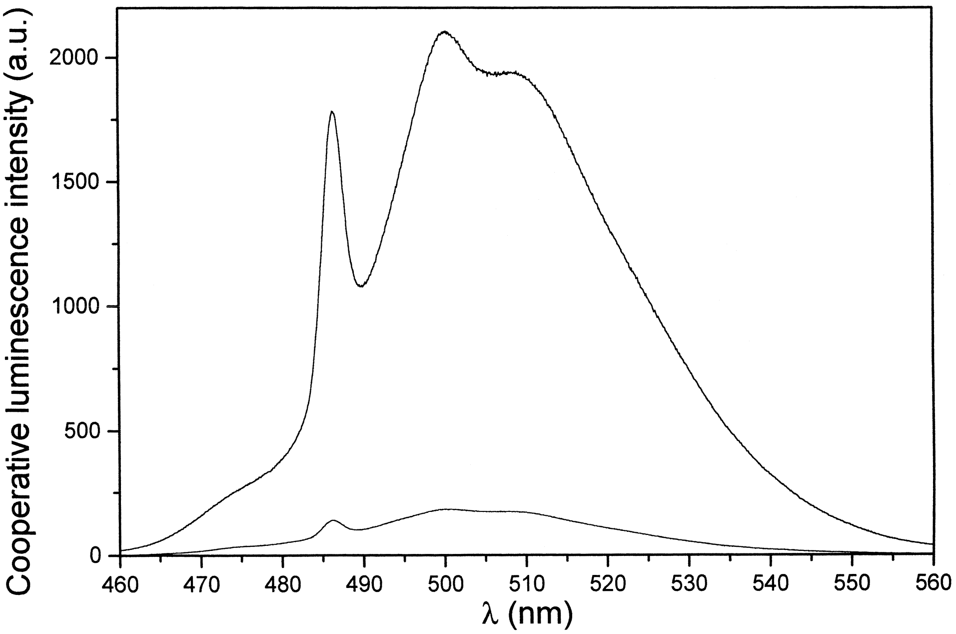

Fig. 6. Cooperative luminescence spectra of aluminosilicate glasses with two different chemical compositions.

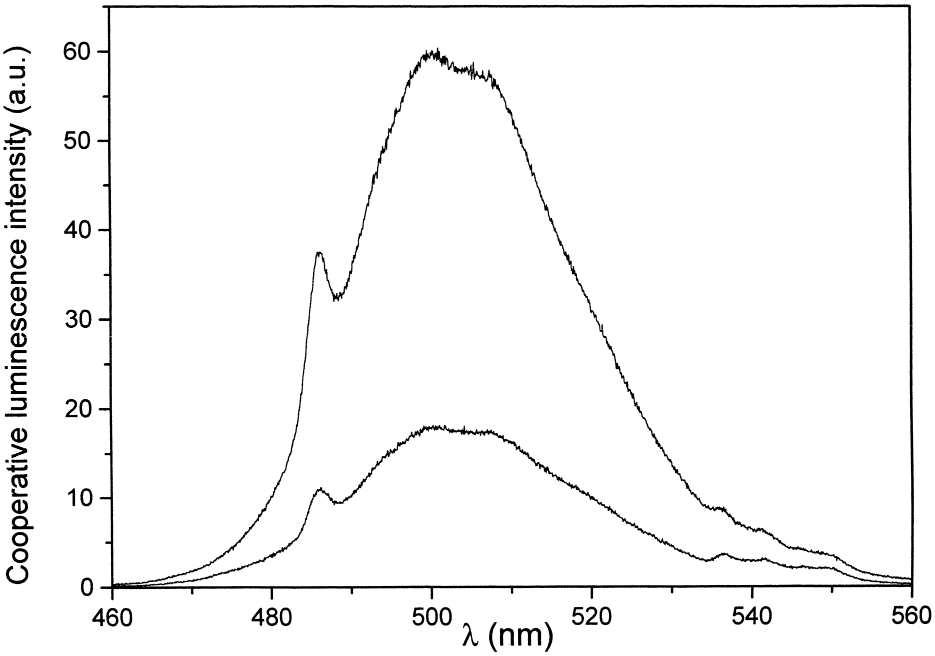

Fig. 7. Cooperative luminescence spectra of borosilicate glasses with two different chemical compositions.

ions. For larger R, clustering is more and more pronounced because end units appear that allow RE ions to get closer. The effect of modifiers on RE clustering is thus opposite to what is observed in pure silica glasses [10]. This is due to the rigidity of the $[SiO_4]^{4-}$ network in which RE ions do not easily enter whereas the $[PO_4]^{3-}$ network can accept large RE concentration.

## 5. Conclusion

Cooperative luminescence has been observed around 500 nm in $Yb^{3+}$ doped aluminosilicate, borosilicate and phosphate glasses. The nature of this emission has been confirmed by infrared luminescence spectrum convolution and lifetime measurements. Possible contribution to the

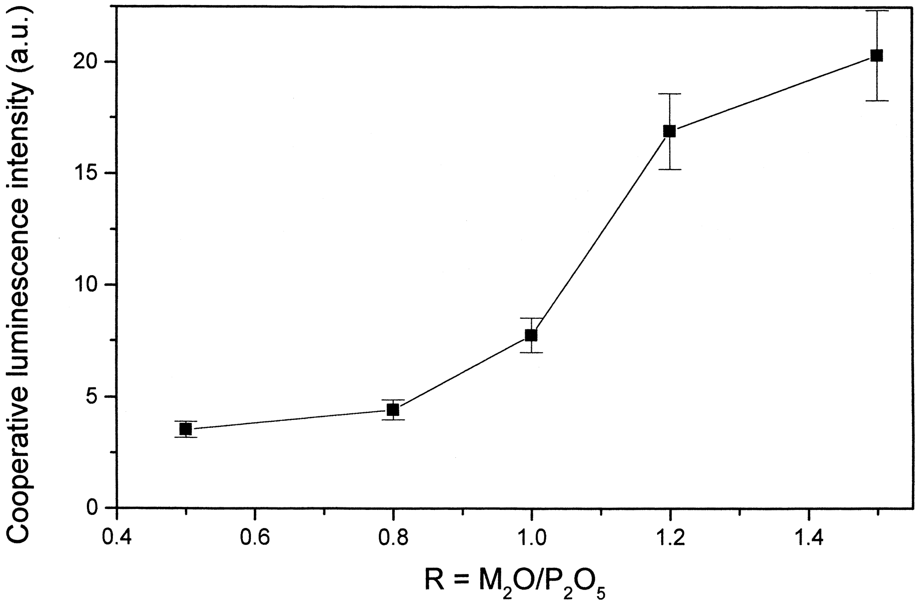

Fig. 8. Evolution of the cooperative luminescence intensity at 510 nm versus $R=M_2O/P_2O_5$ in phosphate glasses.

cooperative luminescence intensity from erbium and thulium ions has also been investigated and found to be negligible at 500 nm.

Examples of the variation of the cooperative luminescence with chemical composition are presented for alumino and borosilicate glasses. A systematic study of cooperative luminescence has also been performed on phosphate glasses ($Li_2O$–$MgO$–$P_2O_5$) with respect to the modifier-former ratio. The cooperative emission intensity increases with increasing modifier content, indicating that the $[PO_4]^{3-}$ network isolates RE ions and its depolymerisation favours clustering.

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## References

[1] E. Nakazawa, S. Shionoya, Phys. Rev. Lett. 25 (1970) 1710.

[2] V.V. Ovsyankin, I.G. Podkolzina, A.A. Fedorov, Izv. Akad. Nauk SSSR 43 (1979) 1194.

[3] M.P. Hehlen, H.U. Güdel, J. Chem. Phys. 98 (1993) 1768.

[4] F. Auzel, D. Meichenin, F. Pellé, P. Goldner, Opt. Mat. 4 (1994) 35.

[5] R.T. Wegh, A. Meijerink, Chem. Phys. Lett. 246 (1995) 495.

[6] P. Goldner, F. Pellé, D. Meichenin, F. Auzel, J. Lumin. 71 (1997) 137.

[7] S. Magne, Y. Ouerdane, M. Druetta, J.P. Goure, P. Ferdinand, G. Monnom, Opt. Comm. 111 (1994) 310.

[8] B.J. Ainslie, S.P. Craig-Ryan, S.T. Davey, J.R. Armitage, C.G. Atkins, J.F. Massicot, R. Wyatt, IEEE Proc. 137 (1990) 205.

[9] P. Blixt, J. Nilsson, T. Carlnäs, B. Jaskorzynska, IEEE Photon. Technol. Lett. 3 (1991) 996.

[10] K. Arai, H. Namikawa, K. Kumata, T. Honda, Y. Ishii, T. Handa, J. Appl. Phys. 59 (1986) 3430.

[11] P. Goldner, F. Pellé, F. Auzel, J. Lumin. 72–74 (1997) 901.

[12] J.R. Van Wazer, Phosphorus and its compounds, Chemistry, Vol. 1, Interscience, New York, 1958.