

# Decay kinetics and energy transfer in ternary phosphate glass doped Eu and Eu/Dy

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**Abstract.** Different series of glass samples with different glass compositions and different concentrations of rare earth ions (Eu and Eu/ Dy co-doped) were prepared. Excitation and photoluminescence spectra were measured, for which the observed peaks are attributed to the  $f-f$  transitions of the rare earth ions. Decay kinetics of the characteristic emission peaks were registered and investigated using Inokuti–Hirayama model (IH model), when the emission decay deviated from the exponential pattern to study energy transfer in the prepared samples. The IH model is used to determine the energy transfer parameter which is correlated to the glass composition factor.

## 1. Introduction

Rare earth ions find wide applications in sensitizing solid state and glass lasers, infrared quantum counters as well as infrared to visible converters. Energy transfer between ions in solids can be accomplished either radiatively or nonradiatively and the mechanism and kinetics involved have been extensively addressed [1, 2]. Many workers have treated the radiative and nonradiative transitions in the rare earth ions and succeeded in realizing energy transfer process in doubly doped crystals and glasses [3–6]. In particular, the excellent work by Blasse and coworkers has resulted in the elucidation of energy transfer, energy migration and concentration quenching in various rare earth ions [7–10]. One important consequence of the energy transfer process is the phenomenon of sensitized luminescence in solids. It is an important factor in increasing the laser efficiency of the materials. Hence this phenomenon has a significant application in the research and development of new laser materials and it is possible to remarkably reduce the threshold energy of laser oscillation in these materials. A large number of studies on sensitized luminescence or fluorescence and concentration quenching have been made, since the wide spread interest results from the breadth of research areas encompassed by the phenomena of energy transfer [11,12].

## 2. Experimental

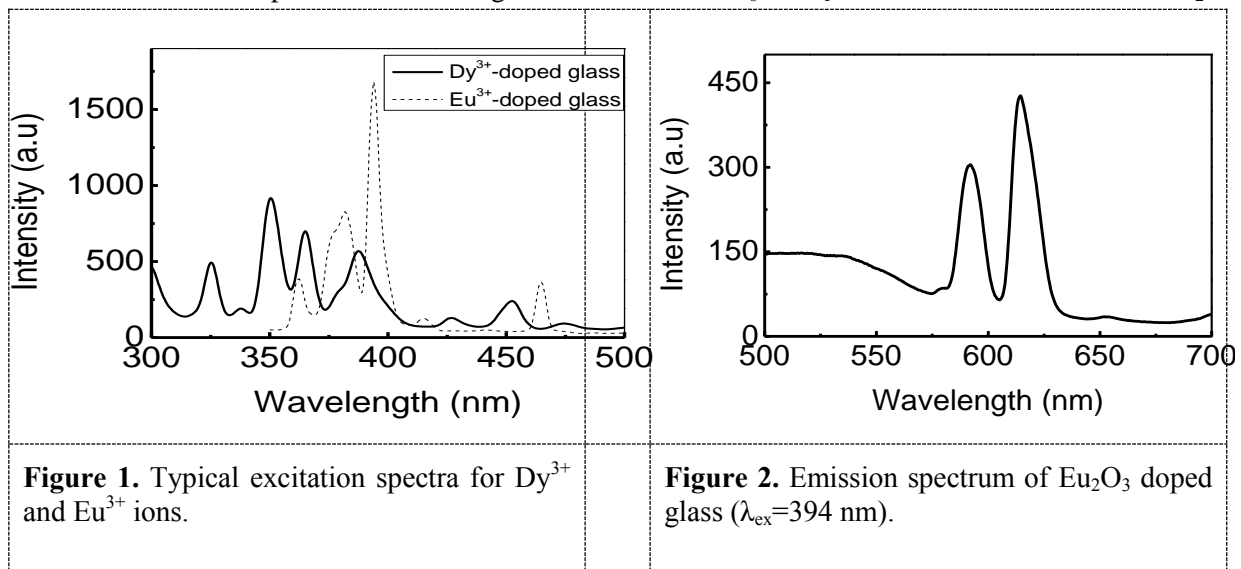
For the current work, two glass systems namely; series (B) of composition  $50\text{P}_2\text{O}_5 - x\text{ZnO} - (50-x)\text{Li}_2\text{O}:5\text{wt}\%\text{Eu}_2\text{O}_3$  and series (C) of composition  $50\text{P}_2\text{O}_5 - x\text{ZnO} - (50-x)\text{Li}_2\text{O}:1\text{wt}\%\text{Eu}_2\text{O}_3+3\text{wt}\%\text{Dy}_2\text{O}_3$  is prepared from high purity chemicals (Aldrich chemicals), using the melt-quench technique, where  $x$  changes in steps of 10, and ranging from 0 to 50 mol%. Photoluminescence and excitation spectra were recorded at room temperature using a Jasco spectrophotometer FP-777. Emission decay kinetics were recorded using a system of monochromator MDR-3 and GW-Instec GDS-2204



oscilloscope for signal detection, and a Xenon pulsed lamp of about 150 $\mu$ s pulse duration for excitation.

### 3. Results and discussion

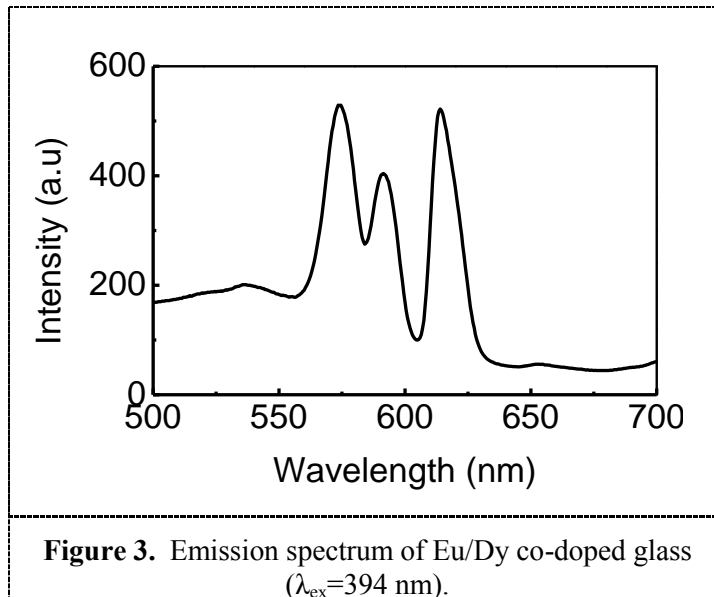
Excitation spectra of samples under study (fig.1.) , were measured in the range 300-500 nm. Where spectrum of the Dy<sup>3+</sup> doped glasses results from the f-f transitions as follows; from <sup>6</sup>H<sub>15/2</sub> to <sup>4</sup>P<sub>7/2</sub> (350nm), <sup>6</sup>P<sub>3/2</sub> (356), <sup>4</sup>F<sub>7/2</sub> (388), <sup>4</sup>G<sub>11/2</sub> (425) and <sup>4</sup>H<sub>15/2</sub> (452). While for the Eu<sup>3+</sup> ions the first excited state namely <sup>7</sup>F<sub>1</sub> is thermally populated at room temperature so the excitation spectrum consists of transitions from the <sup>7</sup>F<sub>0</sub> and <sup>7</sup>F<sub>1</sub> to the higher excited states. Peak centered at 394nm which results from the transition <sup>7</sup>F<sub>0</sub> to <sup>5</sup>L<sub>6</sub> of Eu<sup>3+</sup> is the most intensive and was chosen as excitation wavelength in the measurements of the stationary photoluminescence spectra of the two glass systems under study. Photoluminescence spectra shown in Fig.2., consist of the <sup>5</sup>D<sub>0</sub> to <sup>7</sup>F<sub>1</sub> transition at 592 nm and to <sup>7</sup>F<sub>2</sub> at



614 nm transitions of the Eu<sup>3+</sup> ions, in case of singly doped glasses. While in case of Dy/Eu co-doped glasses (Fig.3) the 394 nm excitation line pumps the <sup>4</sup>F<sub>7/2</sub> of Dy<sup>3+</sup> Level results in a transition from the <sup>4</sup>F<sub>9/2</sub> to <sup>6</sup>H<sub>13/2</sub> component of the <sup>6</sup>H<sub>j</sub> ground state of Dy<sup>3+</sup> ion, at 575 nm in addition to the characteristic emission peaks of the Eu<sup>3+</sup> ions.

Studying the decay patterns of the Eu<sup>3+</sup> emission at its characteristic <sup>5</sup>D<sub>0</sub> to <sup>7</sup>F<sub>1</sub> transition, for different glass composition shows that: in case of Eu<sup>3+</sup> singly doped glasses emission signals decay are ideal exponentials as shown in Fig.4.a. Using a single exponential fitting, the decay times are calculated for this series and are presented in Fig.5. In the case of double doping, decay patters (Fig.4.b.) deviated from the ideal exponential and the calculated decay times presented in Fig.5. for this series show a drastic decrease in its values compared to that in case of singly doped glasses. The above mentioned observations lead us to suggest an energy transfer from the Eu<sup>3+</sup> excited ions to Dy<sup>3+</sup> ions, this leads to deexcitation of the Eu<sup>3+</sup> ions via non-radiational transition so increasing the decay time of the species and that this energy transfer depends on the composition of the glass matrix. When the interaction between rare earth ions is not important, decay curves can be described using single –exponential function to obtain the lifetime of the emitting level.

When energy transfer between the dopant ions appears and the decay curves show a non-exponential



**Figure 3.** Emission spectrum of Eu/Dy co-doped glass ( $\lambda_{\text{ex}}=394$  nm).

behavior, expression derived by Inokuti and Hirayama (Widely known as IH model) [13], for the decay of luminescence of a donor-acceptor system can be used.

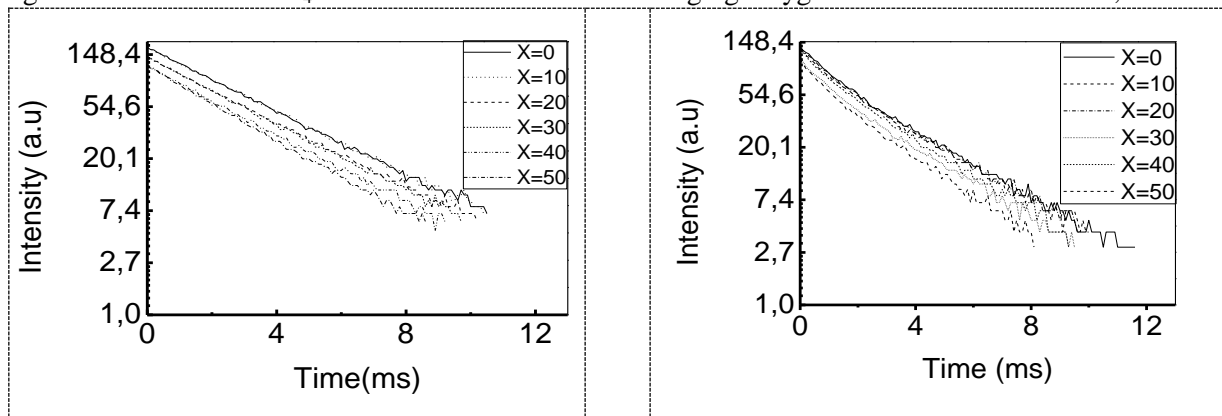
In the IH model, emission intensity as a function of time is given by

$$I(t) = I_0 \exp \left\{ -\frac{t}{\tau_0} - Q \left( -\frac{t}{\tau_0} \right)^{\frac{3}{s}} \right\}$$

Where,  $t$  is the time after excitation,  $\tau_0$  is the intrinsic decay time of the donors in the absence of acceptors.  $Q$  is the energy transfer parameter. The value of  $s$  depends on the type of energy interaction, with  $s=6, 8, 10$  for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interaction

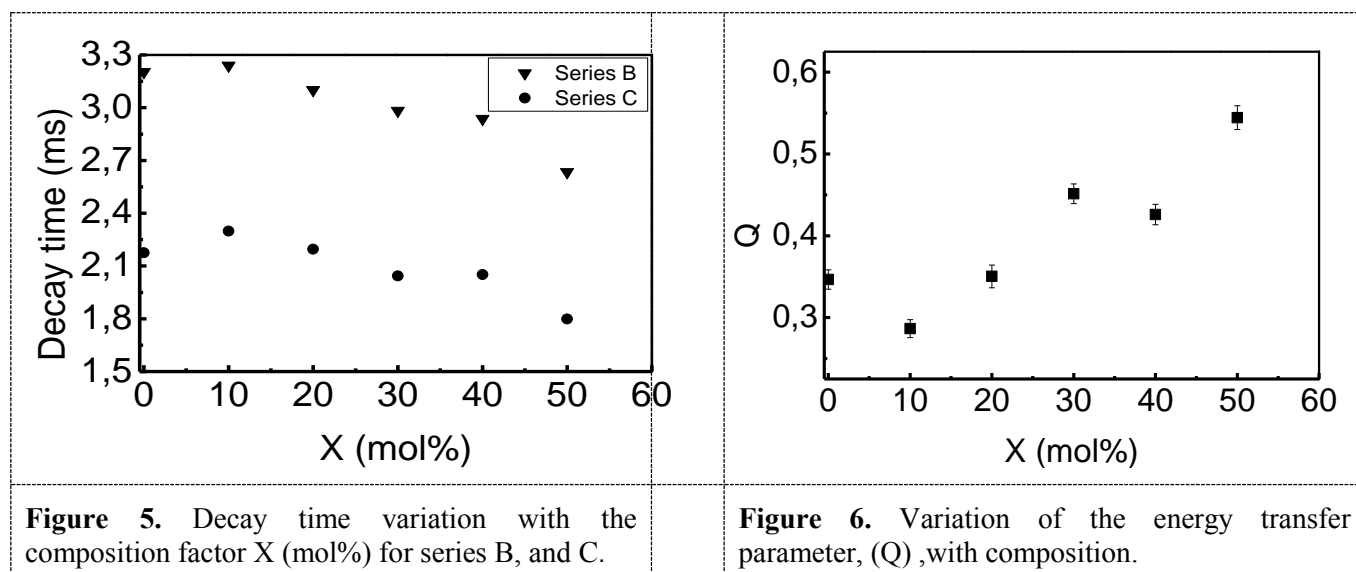
respectively.

To study the nature of energy transfer processes between  $\text{Eu}^{3+}$ , and  $\text{Dy}^{3+}$  ions responsible for the non-exponential decay pattern. The behavior of the decay curves has been analyzed in the frame work of the Inokuti-Hirayama model. A good fitting using IH model with  $s=6$ , reveals that the energy transfer is dipole-dipole in nature and the obtained values of the energy transfer parameter ( $Q$ ) which are presented in fig.6., show dependence on the composition of the glass matrix. Lifetimes of the  ${}^4\text{F}_{9/2}$  level are found to decrease with the composition factor  $x$ . suggesting that the consequent replacement of  $\text{Li}_2\text{O}$  by  $\text{ZnO}$  enhances the process of energy transfer between the rare earth ions.  $\text{P}_2\text{O}_5$  based glasses consists of  $\text{PO}_4$  tetrahedra connected via bridging oxygen ions with P-O bonds, and one



**Figure 4** PL Decay patterns of  $\text{Eu}^{3+}$  emission for series B (left), series C (right) of  ${}^5\text{D}_0$  to  ${}^7\text{F}_1$  transition ions.

dangling double bonded oxygen ion (non-bridging oxygen), from our previous work, using IR investigation of similar glass composition [15] we found that the addition of  $\text{ZnO}$  to glass composition creates additional non-bridging oxygens. So we could conclude that the replacement of  $\text{Li}_2\text{O}$  by  $\text{ZnO}$  results in an increase of non-bridging oxygens. The existence of which increases the covallency of RE-O bonds, and enhance the RE site symmetry which may lead to enhancement of energy transfer.



#### 4. Conclusion

It could be concluded that co-doping of RE ions affects the emission characteristics of the glass with introducing the emission lines of the co-doped ion and that the possibility of energy transfer between the RE ions effectively affect the emission decay time, where the decay time of the  $\text{Eu}^{3+} \ ^5\text{D}_0\text{-}^7\text{F}_1$  transition decreased from about 3 ms in case of  $\text{Eu}^{3+}$  singly doped glasses to about 2 ms. In the case of co-doping Where the IH model could give insight about the mechanism of the energy transfer and the good agreement of the model proposed by Inokuti and Hirayama gives the opportunity to calculate the energy transfer parameter, which we found to depend on the glass composition.

#### 5. References

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