Study of optical interaction between UO_2^{++} and Ho^{3+} in zinc phosphate glass

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A study of Non-radiative energy transfer in UO_2-Ho system in zinc phosphate glass has been done by observing the steady state emission of UO_2^{++} with varying concentration of Ho^{3+} in zinc phosphate glass at room temperature. It has been observed that UO_2^{++} ion emission intensity decreases with increasing Ho^{3+} concentration resulting in a non-radiative energy transfer from UO_2^{++} to Ho^{3+}. The energy transfer mechanism for the systems is confirmed to be electric dipole-dipole in nature according to Fong-Diestler's, Forster and Dexter's and Van Uitert's theory. The donor-acceptor distances ($D_{D \to A}$) and transfer efficiencies (η), as well as energy transfer probabilities (P_{da}) in presence of different acceptor concentration, have been calculated.

Keywords: Rare earth ions, Non-radiative energy transfer, Dipole-dipole interaction, Zinc phosphate glass.

Introduction

Rare earth (RE) doped materials have been extensively investigated due to their vast and significant applications for LASER hosts, luminescent applications, sensors, lamp phosphors, broadband amplifiers, optical data storage devices and optical fiber communication system[1-4]. In recent years considerable progress has been achieved toward improving the pumping efficiency of solid-state lasers containing trivalent rare earth ions as active agents. One approach, which will be particularly useful, is based on the sensitization of active rare earth ions by uranyl ion. The uranyl ion (UO_2^{++}) has its maximum emission in the green region. The probability of energy transfer from uranyl ions to other ions particularly to RE ions is high so uranyl ion has found its application in various fields such as indirect pumping source application for RE ions in lasers, luminescence, photochemical reactions, studying the nature of excited state solar energy converters[5-7].

The transfer of optical excitation energy from one ion/molecule to another ion /molecule is of immense importance in the industrial application as well as in research in recent past years. The theory of non-radiative energy transfer from one ion (donor) to another ion (acceptor) has been discussed in detail by

several authors[8-16]. In the development of the rare earth doped optical device, the choice of the host glass matrix is a very important factor to be considered. In glass matrices, due to inhomogeneous broadening of the doped ion levels, the probability of energy transfer increases[17]. Oxide-based phosphate glasses have unique physical and chemical properties including higher electrical conductivities, high mechanical strength, and optical transparency, which make them the potential for various applications such as in high energy laser applications, fiber amplifiers, solid-state batteries and sealing glasses[18-20]. Hence zinc based phosphate glasses can be considered as promising materials for applications in optoelectronics.

Holmium ion has a large number of closely spaced energy levels & strong transitions. Many of them can be used as lasers. Ho^{3+} can be sensitized by various RE or other ions to achieve good laser emission. Uranyl ion is found particularly useful as an indirect pumping source for RE ions because its emission occurs from an excited level situated at around 20200 cm^{-1}. Joshi *et al.*[21] observed energy transfer from UO_2^{++} to Eu^{3+} in H_2O, D_2O, potassium formate, and acetic media. They found that a small portion of energy lost by uranyl ions is transferred to Eu^{3+} ion via the non-radiative process. Energy transfer between UO_2^{++} and Eu^{3+} in several solutions has been observed by John L. Kropp[22]. Transfer of energy from UO_2^{++} to

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Sm^{3+} in zinc phosphate glass has been studied by Joshi *et al.*[23]. Energy transfer from UO_2^{++} to Er^{3+} and UO_2^{++} to Eu^{3+} in different glass matrices has also been reported by other workers[24,25]. The earlier investigations by C.C. Dhondiyal *et al.* have done on Eu-Tm, Dy-Eu, Eu-Er, Tb-Er, Sm-Er, and Tb-Ho systems in zinc phosphate glass[26-31]. Keeping the above points in mind we have taken Ho^{3+} as acceptor and uranyl ion as a donor ion. To the best of our knowledge, no work has been done on UO_2-Ho system in zinc phosphate glass. The present paper aims to find out the possibility of non-radiative energy transfer from UO_2^{++} to Ho^{3+} as well as mechanism of energy transfer between UO_2^{++}-Ho^{3+} in zinc phosphate glass. For quantitative measurements various parameters like donor-acceptor distances ($D_{D \to A}$) and transfer efficiencies (η), as well as energy transfer probabilities (P_{da}) in presence of different acceptor concentration, have been calculated.

1 Experimental Details

Reagent grade Sodium dihydrogen phosphate 2-hydrate ($NaH_2PO_4.2H_2O$) (E-Merck, India) and reagent grade zinc oxide (ZnO) (Ferak Berlin, Germany) were mixed in a proportion of 3:1 by weight respectively to prepare the host glass matrix. Uranyl acetate [$UO_2 (C_2H_3O_2.2H_2O$] (phosphor grade) was obtained from Indian rare earth limited, Kerala, while Holmium oxide (Ho_2O_3, 99 % pure) was obtained from GTE Sylvania. For UO_2-Ho series donor (UO_2^{++}) concentration was kept fixed at 0.1 wt% while acceptor (Ho^{3+}) concentration was varied from 0.5 wt% to 2.5 wt%. All the components of the glass with requisite composition were thoroughly mixed with rare earth as required and the homogeneous mixture so obtained was melted in a platinum crucible inside an electric furnace at a temperature about 1213 K for half an hour. The molten mass was taken poured into a brass ring (mold) resting on an aluminum plate. The glass so formed was then allowed to cool at room temperature. In this way, it is possible to get glass samples of almost equal size & surface area. The samples were rectangular and $1 \times 1 \times 3$ cm^3 in dimensions. The fluorescence spectra were taken by exciting the sample with the 365 nm group of mercury lines. A fluorometer using grating monochromator (CEL Model, HM104) dispersion 3.3 nm mm^{-1}, Czerny-turner mounting, with a photomultiplier tube (RCA1P21) and a nanometer were used to scan the spectra. For low-intensity emissions, the grating monochromator was replaced by a constant deviation

prism monochromator. Absorption spectra of zinc phosphate glass were taken by using EC double beam UV-VIS spectrometer (ECILUVS 70455). All spectra were taken at room temperature (20^{0}C). Single-flash technique was used to obtain lifetime data. A high-pressure flash lamp (BH-6 Hg) was used for measuring decay times. The emission was excited by 365 nm radiation. All the observations were carried out at room temperature.

2 Results and Discussion

The emission spectra of UO_2^{++} (0.1 wt %) doped in zinc phosphate glass under 365 nm excitation is shown in Fig. 1(a). As shown in Fig. 1(a), when excited by 365 nm groups of mercury lines uranyl ions gives their characteristic emission in the visible region (green). Figure 1(b) shows the emission spectra of UO_2^{++} in the presence of holmium ion in the host matrix. Because of strong and broad absorption bands in the UV region of the uranyl ion, it has a large oscillator strength compared to trivalent rare earth ions and consequently, a large portion of excitation energy is absorbed by it which can easily be transferred to rare earth ions. A comparison of both curves clearly indicates that the intensity of UO_2^{++} decreases at all wavelengths when it is co-doped with the Ho^{3+} ion. Neglecting the transfer of energy from UO_2 to eligible impurity ion as well as the absence of self-quenching of uranyl ion at this concentration, it is obvious that this energy is transferred to the added Ho^{3+} ion (acceptor) non-radiatively[16]. This result is further supported if we look on Fig. 2, which represents the emission intensity of uranyl ion in the presence of varying concentration of acceptor ion
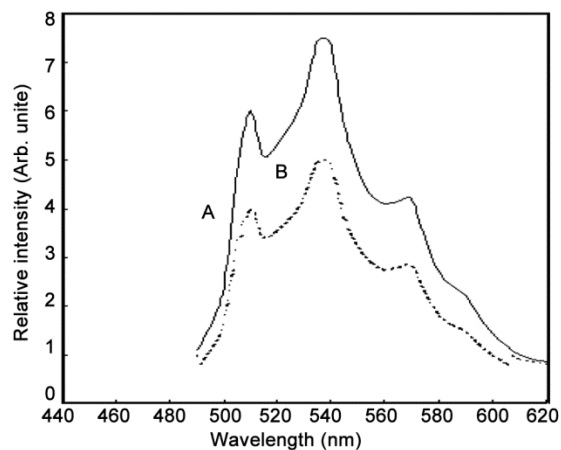

Fig. 1a — Emission spectra of UO_2^{++} (0.1 wt %) in zinc phosphate glass. (b) Emission spectra of UO_2^{++} (0.1 wt %) + Ho^{3+} (1.0 wt %) in zinc phosphate glass.
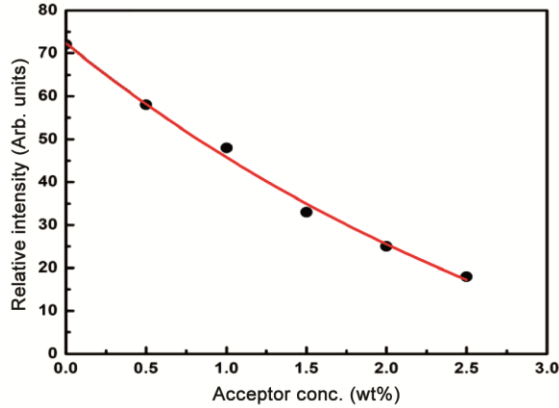
Fig. 2 — Variation of UO$_2^{++}$ emission with varying concentration of Ho^{3+}.

(Ho^{3+}). Figure 2 clearly shows that the emission intensity of uranyl becomes lower and lower with increasing concentration of acceptor ion. The reason for the decrease in emission intensity of uranyl ion with increasing holmium ion is that now more acceptor ions are available to every donor ion to accept its energy. Concentration quenching of uranyl ion was not observed in zinc phosphate glass up to this concentration *i.e.* 0.1 wt%. In the absence of concentration quenching, the overall decrease in donor emission is suggested to be due to non-radiative energy transfer from uranyl to holmium ion[16]. Since the holmium ions have unobservable emission in the visible region in zinc phosphate glass by the excitation radiation (365 nm) the possibility of back transfer of energy from Ho^{3+} to UO$_2^{++}$ is extremely low. Because of the large oscillator strength of uranyl ion also, a large portion of excitation energy goes to the uranyl ion. Non-radiative nature of energy transfer process is also supported by the fact that on increasing Ho^{3+} concentration in the system the decay of UO$_2^{++}$ luminescence becomes faster (Fig. 3).

The mechanism of interaction among the excited ions was first explained by Forster[8], who predicted that the rate of energy transfer is proportional to the overlap of the donor emission and the acceptor absorption spectra. Forster assumed that the interaction between two well-separated ions is strongest if for both the ion's electric dipole transitions are permitted and the energy transfer probability from donor to acceptor is:

$$\eta_d \qquad - \!\!- \qquad\qquad\qquad\qquad \text{… (1)}$$

This shows the R^{-6} dependence of the transfer rate. In this relation, 'R' is the distance between the donor and
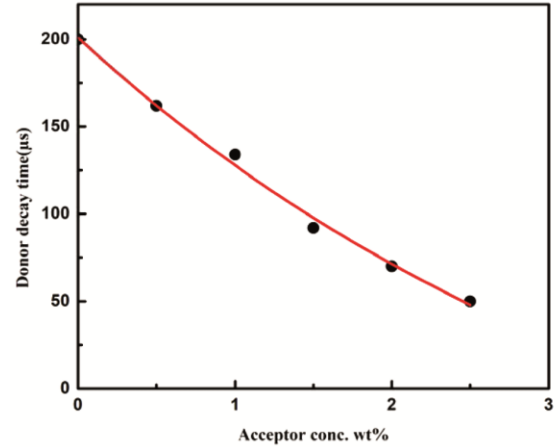

Fig. 3 — Variation of UO$_2^{++}$ decay time with Ho^{3+} concentration at room temperature.

acceptor; τ_d^0 is the radiative lifetime of excited donor and R$_0$ is the critical transfer distance at which the energy transfer probability is equal to the radiative transition probability. Dexter[9] extended Forster's theory and includes the case of forbidden transition moments in donors and acceptors. He shows the radial dependence of the ion pair transfer rate is R^{-6}, R^{-8}, R^{-10} for electric dipole-dipole (EDD), electric dipole-quadrupole (EDQ) and electric quadrupole-quadrupole (EQQ) coupling respectively. Although Dexter is able to explain the concentration dependence of luminescence yield in a reasonable way radial dependences and dominant interactions in some cases are often ambiguous. It was found that in a given material different interactions will dominate for different concentration ranges *i.e.* longer-range interaction for low concentration and short-range (but stronger) interaction for concentration large enough to show substantial ion per decay. In Dexter's theory, it was assumed that luminescence was dominated by the transfer to the nearest acceptor ion. An extension of the entire environment including the dynamics of the transfer was formulated by Inokuti & Hirayama[10]. According to this theory, the emission intensity of the donor decays as a result of electrostatic multipolar interactions with acceptors, when donor & acceptor ions are randomly distributed and the donor ions are excited by a flashlight, according to the following equation:

$$I(t) = \exp\left[-t/\tau_{d0} - \Gamma(1 - 3/S) \cdot C/C_0 \, (t/\tau_0)^{3/S}\right] \qquad \text{… (2)}$$

Where C_0 is the critical acceptor concentration which is given by the relation $C_0 = 3/(4\pi R_0^3)$; τ_{do} is the decay constant of the donor in absence of the acceptor; C is the acceptor concentration; Γ is the

gamma function; R_0 is the critical transfer distance and S is the parameter for electrostatic multipolar interaction which takes the values 6,8 and 10 for dipole-dipole, dipole-quadrupole, and quadrupole–quadrupole interactions, respectively.

In an extended series of investigations on energy transfer processes in single crystals doped with lanthanide ions, Van Uitert and co-workers[11,12] have observed the variation of donor intensity or the lifetime with varying acceptor concentration and used the following relationship for the quantum efficiency:

$$\ldots (3)$$

Where I_0 is the radiative intensity of donor in the absence of acceptor; I is the radiative intensity in the presence of acceptor at acceptor concentration 'C' and β is a constant. According to Van Uitert theory if a curve is plotted between $\log(I_0/I_{ob} - 1)$ and $\log(C/C^{*})$ (where, I_0 is the emission intensity of the donor ion in the absence of acceptor; I_{ob} is the emission intensity of the donor ion in the presence of acceptor; C is acceptor concentration;

— and R^{*} is critical transfer distance between donor and acceptor ions.) it comes out to be a straight line whose slope is $\theta/3$. This can be used to study the multipolar term responsible for interaction between donor and acceptor ion. According to Van-Uitert theory, the value of θ is 6,8,10 for electric dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively.

Fong and Diestler[16] consider that many body interactions can play a dominant role in non-radiative energy transfer processes in RE ions. He shows the concentration dependence of non-radiative transfer processes in terms of ensembles of statistical mechanics. According to which, at low donor acceptor concentration the transfer rate per ion varies linearly with the concentration and the transfer occurs by a pair wise (two body) interaction. At higher concentration, a higher order interaction mechanism can take place. In general the per ion transfer rate P_{DA} varies linearly with C^{n-1} where C is the concentration of the donor & acceptor ions and n determines the order of the process.

Figure 4 represents the energy level diagrams[32] of UO_2^{++} and Ho^{3+}. The uranyl ion luminescence from the excited level situated at around 20200 cm^{-1} above the ground state. Now a closer look at the energy level diagram indicates that $^3K_3$ level of Ho^{3+} is very close with the emitting level of UO_2^{++}. Therefore a
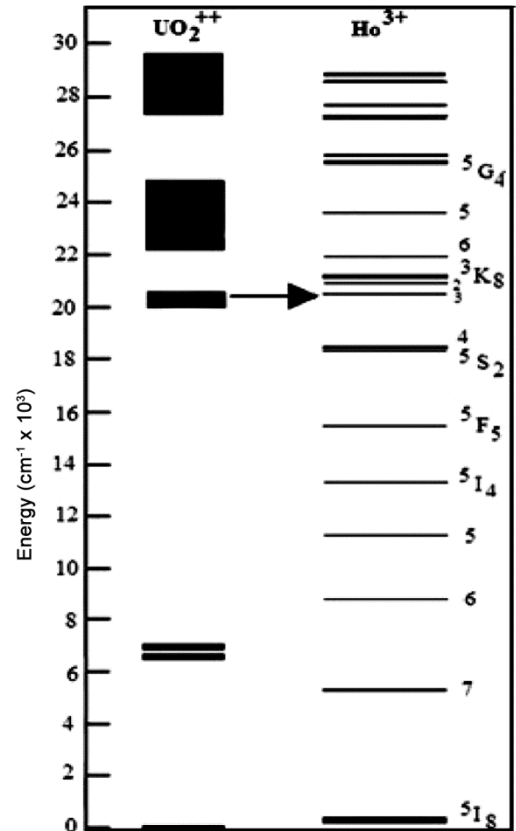

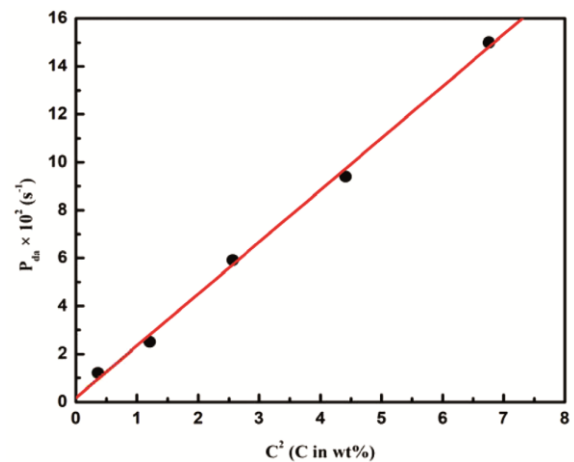Fig. 4 — Energy level diagram of UO_2^{++} and Ho^{3+}.

Fig. 5 — Plot of energy transfer probability (P_{da}) against the square of Donor + acceptor concentration (C^2) for UO_2^{++} - Ho^{3+}.

resonance energy transfer is suggested between these levels *i.e.* the excitation energy of the UO_2^{++} ion is transferred to $^3K_3$ levels of Ho^{3+}. It causes a decrease in UO_2 emission. In order to find out which multipolar term is responsible for energy transfer from UO_2^{++} to Ho^{3+}, we use Fong-Diestler theory[16]. So we have drawn a curve (Fig. 5) between P_{da} & C^2, where P_{da} is

Table 1 – Effect of acceptor concentration on average donor-acceptor distances, energy transfer efficiencies and energy transfer probabilities for the UO$_2$$^{++}$-Ho^{3+} system at donor concentration 0.1 wt%.

C$_{donor}$ (wt%)	C$_{acceptor}$ (wt%)	τ_0 (µs)	τ (µs)	I$_{do}$ ($\pm$1)	I$_d$ ($\pm$1)	D$_{D-A}$ (nm$\pm$0.1)	η ($\pm$0.05)	P$_{da}$×10^3 (s^{-1} $\pm$0.05)
0.1	0.5	200	162	72	58	2.89	0.19	1.21
	1.0		134		48	2.36	0.33	2.50
	1.5		92		33	2.08	0.54	5.91
	2.0		70		25	1.90	0.65	9.40
	2.5		50		18	1.77	0.75	15.0

Where C$_{donor}$ is the donor concentration; C$_{acceptor}$ is the acceptor concentration; τ_0 is the intrinsic donor decay time; τ is the donor decay time in the presence of acceptor; I$_{do}$ is the donor intensity in the absence of acceptor; I$_d$ is the donor intensity in the presence of acceptor; D$_{D-A}$ is the average donor- acceptor distance; η is the energy transfer efficiency; and P$_{da}$ is the energy transfer probability.

the probability of energy transfer between donor and acceptor ions and C is the (donor + acceptor) concentration. The linear dependence of P$_{da}$ on the square of the concentration of donor + acceptor shows that P$_{da}$ is directly proportional to 6th power of radius hence dipole-dipole interaction[16] between donor and acceptor is mainly responsible for energy transfer between UO$_2$$^{++}$ and Ho^{3+}.

Table 1 represents some of the parameters necessary to analyze the energy transfer from UO$_2$$^{++}$ to Ho^{3+}. The average donor-acceptor distance was calculated by using the formula:
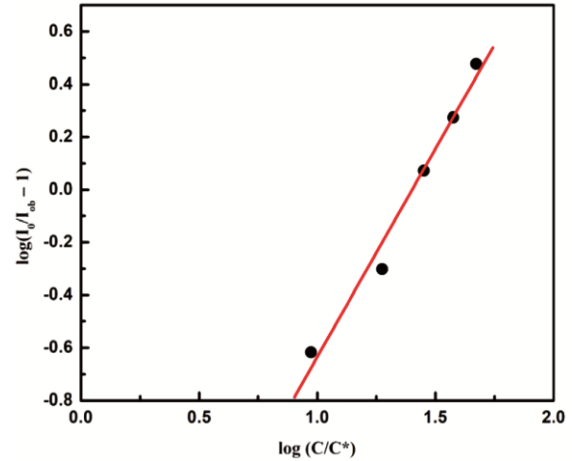
$$\dots (4)$$

Where C$_d$ and C$_a$ are donor and acceptor ion concentration per cm^3 in the host matrix. The energy transfer efficiencies and the transfer probabilities were calculated by using the following relation[33,34]:

$$ \qquad \dots (5)$$

$$ \qquad \dots (6)$$

Where, I$_{do}$ is the donor intensity in the absence of acceptor; I$_d$ is the donor intensity in the presence of acceptor; τ_0 is the intrinsic donor decay time; τ is the donor decay time in the presence of acceptor, η is the energy transfer efficiency and P$_{da}$ is the energy transfer probability.

The dipole-dipole mechanism of energy transfer is further supported by the average donor to acceptor distance which varies in this system from 2.89 to 1.77 nm (Table 1) and falls in dipole-dipole interaction range in accordance with Forster's and Dexter's theories[8,9] of multipolar interactions. Energy transfer by exchange process is not possible in this case because it needs a donor-acceptor ion separation of

Fig. 6 — Relationship between log (I$_0$/I$_{ob}$-1) and log C/C* for UO$_2$$^{++}$-Ho^{3+}.

about 0.3-0.4 nm with considerable overlap of wave functions. Dipole-dipole interaction is further corroborated by using Van Uitert theory[11,12]. The curve plotted between log (I$_0$/I$_{ob}$-1) and log (C/C*) has been presented in Fig. 6 which comes a straight line indicating a multipolar interaction between UO$_2$$^{++}$ and Ho^{3+}. The slope of the line *i.e.* θ/3 is approximately coming out to be 2 which gives a value of around 6 to θ, suggesting the dipole-dipole interaction between donor and acceptor ions.

Table 1 shows that the energy transfer efficiency (η) in the UO$_2$$^{++}$- Ho^{3+} system increases from 0.19 to 0.75 as well as transfer probability (P$_{da}$) increases from 1.21 × 10^3 to 15.0 ×10^3 s^{-1} respectively. This shows that with increasing concentration of holmium ion emission intensity of Ho^{3+} can be enhanced by energy transfer. The critical transfer distance (R$_0$) in the UO$_2$$^{++}$- Ho^{3+} system is 2.12 nm which can be compared with those obtained by Joshi *et al.*[35,36] R$_0$=1.91 nm in Dy-Ho and 1.65 nm in Tm–Ho system

in zinc phosphate glass and by Joshi *et al.*[37] 1.29 nm in Tb-Ho system in the calibo glass.

3 Conclusion

The paper investigates the energy transfer from UO_2^{++} to Ho^{3+} in zinc phosphate glass by keeping donor concentration fixed and varying the acceptor concentration. The mechanism of energy transfer is found non-radiative energy transfer involving dipole-dipole interaction between donor-acceptor. Fong-Diestler theory[16] is used to explain the dipole-dipole interaction. Dipole-dipole interaction between the donor-acceptor pair is further supported by Forster and Dexter's theory[8,9] and Van Uitert's theory[11,12]. Resonance energy transfer is suggested as the $^3K_3$ level of Ho^{3+} is very close with the emitting level of UO_2^{++}. The electric dipole-dipole interaction is quantitatively analyzed by calculating the donor-acceptor distance $(D_{D \to A})$ & critical transfer distance (R_0). Other energy transfer parameters have also been calculated which show that the transfer is mainly electric dipole-dipole in nature. The emission intensity of Ho^{3+} can be enhanced by energy transfer, which can be used as a laser material.

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