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Nonradiative energy transfer and ion-ion interactions in terbium-praseodymium coactivated borate glass

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ABSTRACT

A study of energy transfer between Tb^{3+} and Pr^{3+} in borate glass is being presented. From our measurement of fluorescence emission and decay times of donor (Tb^{3+}), in the presence of different concentrations of acceptor (Pr^{3+}), the energy transfer probability (P_{da}) and transfer efficiency (η_T) have been calculated. Analyzing the data it is observed that the non-radiative energy transfer in our borate glass system occurs by dipole-dipole interactions, contrary to the observations made by Nakazawa and Shionoya (dipole-quadrupole interaction) in phosphate glass. A linear dependence of P_{da} versus C at low acceptor concentration suggests the migration of excitation energy among donor ions before the energy is finally transferred to the acceptor ion. At high acceptor concentrations a plot of P_{da} *vs* $(C_0 + C)^2$; where C_0 is donor concentration and C is the acceptor concentration, presents a linear dependence suggesting thereby that one donor interacts with two neighbouring acceptors consistent with Fong-Diestler mechanisms of dipole-dipole energy transfer interactions.

1. Introduction

Recent years have seen a spate of activities in the fluorescence energy transfer, energy dissipation and excited state dynamics of rare earth doped materials due to their versatilities and vast applications in the field of lasers, infrared quantum counters, infrared-to-visible converters,

fibre optics, scintillating materials, lamp phosphors and numerous other applications [1]. Although the energy transfer processes between like and unlike ions are better understood at the present state of investigations, yet the emerging trends like excited state absorption, energy transfer upconversion, photon avalanche upconversion and other excited state processes are of paramount importance in designing lasers suitable for specific purposes [2]. Rare earths possessing a large number of energy levels and many metastable states are highly suitable for the laser operation not only in the visible region but in the ultraviolet and infrared too, so as to tailor them for the desired needs.

The classical theory of energy transfer was developed by Forster [3] considering dipole-dipole interactions and later on by Dexter [4] for electrostatic multipolar interactions. Inokuti and Hirayama [5] treated the problem on the basis of the nearest-neighbour interactions taking into account the exchange process. The diffusion of optical excitation among donors has been treated in some detail by Yokota and Tanimoto [6] whereas the energy migration among donors in a random hopping manner has been discussed by Weber [7] and Burshtein [8]; a more interesting theory developed by Fong and Diestler [9] treats the interaction from many particle viewpoints.

VanUitert *et al.* [10] observed energy transfer from Tb^{3+} to Pr^{3+} in scheelites of the type $NaWO_4$, $SrNaWO_4$, $BaNaWO_4$ etc.; the mechanism governing the transfer being dipole-quadrupole in nature. Nakazawa and Shionoya [11] in their investigations on Tb-Pr co-doped calcium metaphosphate glass reported that Tb^{3+} to Pr^{3+} energy transfer involves dipole-quadrupole mechanism. Nakazawa and Shionoya [12] later on suggested that the $R^{-3.5}$ dependence of relaxation probability for Tb-Pr interaction in the same glass cannot be explained simply by resonance energy transfer theory but also the migration of excitation energy among donors accelerates the transfer. It was also noted that while the dipole-quadrupole interaction provides the best fit for transfer mechanism, the other fits (e.g. quadrupole-quadrupole etc.) are only slightly beyond the experimental error bars.

The earlier investigations by the second author have mostly been performed by using Nd^{3+}, Ho^{3+}, Er^{3+} as acceptors and Eu^{3+}, Tb^{3+}, Sm^{3+}, Dy^{3+} and UO^{2+} etc. as donor ions [13–20]. Similar studies have also been done by other workers [21,22]. The use of Pr^{3+} as an acceptor ion was not earlier presented by us. The energy levels of Pr^{3+}, being closely spaced, make it interesting to be explored for energy transfer interactions. Keeping the above points into consideration and also in view of the theory developed by Fong and Diestler [9], we have

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studied the energy transfer interaction mechanisms in the Tb-Pr coactivated borate glass system so as to compare with the findings of Nakazawa and Shionoya [11].

2. Materials and methods

Tb-Pr incorporated borate glass samples of base composition Na_2O (30.8%):B_2O_3 (69.2%) were prepared from the starting materials as-disodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) Analar BDH, Terbium oxide (Tb_2O_3) 99.9%, and Pr_2O_3 99.9%, Indian Rare Earths Ltd. The donor (Tb^{+3}) concentration was kept fixed (2.0%) and the acceptor (Pr^{3+}) concentration was varied from 0.5% to 8.0%. The mixed powder containing defined rations of dopants was melted in a platinum crucible for about forty min in an electric furnace at a temperature ~ 1000^0C. The hot melt was poured into a pre-heated metallic ring, resting on an aluminium base, so as to obtain glass discs of almost identical dimensions. The glass samples were inserted inside the same metallic ring fixed on a holder for frontal illuminations in the same geometry for the relative fluorescence measurements.

The glass samples were excited by a 365 nm Hg-lamp (Philips 125 W) covered with Wood's filter. The fluorescent light was analyzed by a prism monochromator SPM-2, Carl Zeiss, Jena and was allowed to fall onto a photomultiplier tube EMI 9558 Q/B. The photocurrent amplified by an electrometer amplifier was fed to a Honeywell chart recorder.

The decay times were measured by a single flash technique using a high pressure mercury lamp BH-6 in combination with a cobalt glass filter for 365 nm irradiation. The flash half width was $< 20\,\mu s$. To select fluorescence bands a prism monochromator was used. The output of the monochromator was fed to a photomultier tube RCA 931 A and the decay pattern was displayed on a Tektronix 502 A dual beam oscilloscope. The decay curves were traced and then analyzed.

3. Results and discussion

Fig. 1 presents the emission spectrum of Tb^{3+} (2.0%) in sodium borate glass at room temperature (300 K). When irradiated by 365 nm group of Hg lines the Tb^{3+} ion is excited directly from $^7F_6$ ground level to the excited ($^5D_3$, $^5G_6$, $^5L_{10}$) levels. The emission bands centred at about 488, 545, 583 and 627 nm are assigned to the fluorescence transitions: $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$, respectively. The most intense bands around 545 nm splits into two Stark components at 543 and 551 nm in sodium borate glass. No emission from $^5D_3$ or higher energy levels of Tb^{3+} could be detected. This is quite feasible in our glass system because the energy gap between $^5D_3$ and $^5D_4$ levels is well matched by two phonons of the borate glass (optical phonon energy 1340–1480 cm^{-1}). Multiphonon emission [23] relaxes the ion quickly to its metastable $^5D_4$ level.

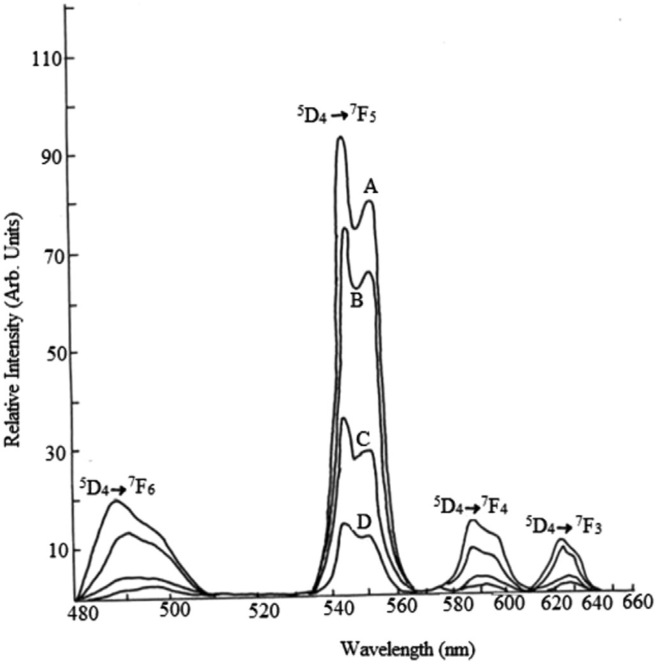

Fig. 1. Fluorescence spectra of: (A)Tb^{3+} (2.0%). (B)Tb^{3+} (2.0%) + Pr^{3+} (1.0%). (C)Tb^{3+} (2.0%) + Pr^{3+} (3.0%). (D)Tb^{3+} (2.0%) + Pr^{3+} (5.0%) in sodium borate glass at room temperature (300^0K), at 365 nm Hg irradiation.

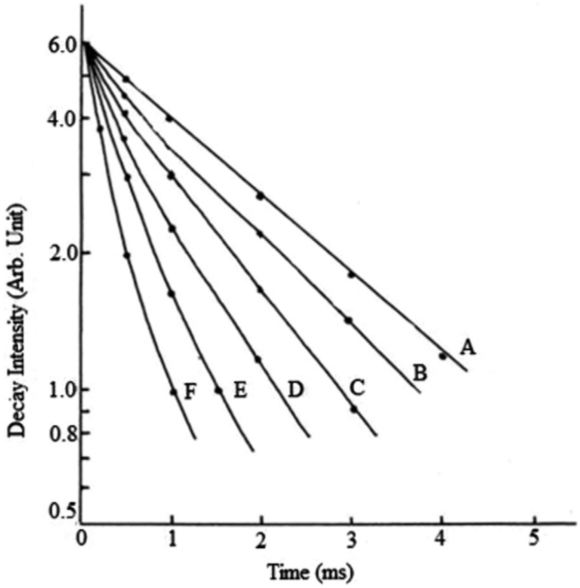

Fig. 2. Decay curves of (2.0%) $Tb^{3+5}D_4$ fluorescence on increasing acceptor concentration. The various concentrations of acceptor (Pr^{3+}) are as under: (A) 0.0%; (B) 2.0%; (C) 3.0%; (D) 4.0%; (E) 6.0% and (F) 8.0%.

The decay time of the $^5D_4$ level of Tb^{3+} (2%) in sodium borate glass was measured as 2700 µs. The analysis of the decay pattern exhibits an exponential character suggesting thereby that the self-quenching is not taking place at this concentration (Fig. 2A).

In order to study temperature dependent relaxation phenomena, the fluorescence intensities and decay times of $Tb^{3+5}D_4$ were also taken at liquid air temperature (80 K). No appreciable changes in emission intensities and lifetimes were observed within the experimental error limits. The observations suggest that the non-radiative decay by multiphonon emission does not make a significant contribution to the Tb^{3+} decay rates even at 300 K [24]. This behavior could be explained on the basis that $Tb^{3+5}D_4$–$^7F_0$ energy gap is too large (14750 cm^{-1}) to be covered by two–three phonons of the borate glass because the energy gap dependence alone determines the multiphonon relaxation.

In sensitized rare earth doped system, the three main processes affect the donor lifetime: (i) intrinsic donor radiative and non-radiative de-excitation, (ii) direct energy transfer from donor to acceptor ions, (iii) diffusion or migration of excitation energy among donor ions followed by its transfer to acceptors. The decay pattern, therefore, manifests different time dependences which provide information about the operative relaxation processes [7].

Fig. 1 (B,C, D) represent the fluorescence spectra corresponding to Tb^{3+} (2%) with co-dopant (Pr^{3+}) (1%, 3%, 5%) w/w, respectively, in sodium borate glass. The observed decrease in the luminescence intensity is attributable to energy transfer from Tb^{3+} to Pr^{3+}. The non-radiative energy transfer is supported by the fact that on increasing Pr^{3+} content in the system, the Tb^{3+} $^5D_4$ decay time falls continuously as is evident from Fig. 2B, C, D. In a typical sample containing 8% Pr^{3+} the decay time of Tb^{3+} drops down to 800 µs. Further the analysis of