Energy transfer between optically excited Tb$^{3+}$ and Er$^{3+}$ ions in zinc phosphate glass

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Received 7 November 2007; revised 1 August 2008; accepted 9 September 2008

A study of energy transfer from optically active ions Tb$^{3+}$ to Er$^{3+}$ in zinc phosphate glass has been made. The evidence of non-radiative energy transfer has been noted from the decrease of Tb$^{3+}$ emission with increasing Er$^{3+}$ concentrations. Energy transfer mechanism is mainly found to be electric dipole-dipole in nature. Various parameters such as energy transfer probability, transfer efficiency and average donor-acceptor distances have been computed.

Keywords: Energy transfer, Sensitization, Fluorescence, Donor, Acceptor, Rare earths

1 Introduction

The luminescence of rare earth ions in glass has been subject of interest since the advent of lasers because sharp bands occur under proper excitation. Since in the rare earths ions the electronic transitions occur within the inner shielded 4-f electron, their spectroscopic properties are not influenced by their surroundings and therefore generally shift in emission bands do not occurs in glass of varying nature. Energy transfer between rare earth ions to rare earth ions find wide application in sensitizing solid state and glass lasers, infrared quantum counters as well as infrared to visible converters.

Joshi et al. reported diffusion limited energy transfer from Tb$^{3+}$ to Ho$^{3+}$ ions in sodium phosphate glass at low acceptor concentration and electric dipole-dipole interaction at high concentration. Joshi et al. have also reported energy transfer from Mn$^{2+}$ to Er$^{3+}$ in phosphate glass due to dipole-dipole interaction between donor and acceptor ions.

In this paper the Tb$^{3+}$- Er$^{3+}$ system in zinc phosphate glass is chosen for observing energy transfer mechanism and for quantitative studies of energy transfer parameters.

2 Experimental Details

The glass matrix was prepared from reagent grade mixture of sodium dihydrogen phosphate-2 hydrate (Na$_2$HPO$_4$·2H$_2$O) (E. Merk, India Ltd.) and zinc phosphate (ZnO) (Ferak Berlin, Germany) in a proportion of 3:1 by weight. Terbium oxide (Tb$_2$O$_3$, 99%) and erbium oxide (Er$_2$O$_3$) are obtained from GTE Sylvania, USA. Single and double doped rare earth ions glass sample were prepared by mixing the chemicals and heating upto 950°C for one hour in an electric furnace and pouring the molten mixture directly into a metal cast resting over an aluminum base.

Emission spectra were taken by frontal excitation of sample with 365 nm group of mercury lines. A grating monochromator (CEL, model HM104) of dispersion 3.3 nm/mm and photomultiplier tube (RCA 1P21) connected to current meter (least count 1 × 10$^{-9}$ amp) were used to scan the spectra. All the spectra are taken at room temperature. Absorption spectra of Er$^{3+}$ (1wt %) in zinc phosphate is taken using EC double beam UV-VIS spectrometer (ECILUV70455) at room temperature. Glass sample of size 1 cm × 1 cm × 3 cm with Er$^{3+}$ ion doped and undoped (reference sample) were prepared for this purpose.

3 Results and Discussion

The emission spectra of Tb$^{3+}$ (1wt %) and Tb$^{3+}$ (1wt %) + Er$^{3+}$ (0.6wt %) are shown in part A and part B of the Fig. 1 respectively. The four peaks of Tb$^{3+}$ arise due to $^5D_4$-$^7F$ manifold transitions. Emission spectra from $^5D_3$ level were not observed due to high Tb$^{3+}$ concentration and perhaps ions previously excited to $^5D_3$ level cross relaxed to $^5D_2$ level.

Figure 2 shows the graph between Tb$^{3+}$ emission intensity with varying Er$^{3+}$ concentration. Energy
level diagrams of $\text{Tb}^{3+}$ and $\text{Er}^{3+}$ are shown in Fig. 3. The plot between energy transfer probabilities ($P_{\text{da}}$) and square of donor concentration + acceptor concentration ($C^2$) is shown in Fig. 4. In Fig. 5 absorption spectra of $\text{Er}^{3+}$ is shown.

Various parameters such as donor-acceptor distances, energy transfer probabilities and energy transfer efficiencies are presented in Table 1. As shown in Figs 1(B) and 2, the overall emission of $\text{Tb}^{3+}$ decreases when doped along with $\text{Er}^{3+}$ ions. Such an overall decrease in donor emission indicates that there is non-radiative energy transfer from $\text{Tb}^{3+}$ to $\text{Er}^{3+}$. This decrease of $\text{Tb}^{3+}$ emission is more pronounced with increasing $\text{Er}^{3+}$ concentration. This decrease in $\text{Tb}^{3+}$ emission can be explained as, on increasing $\text{Er}^{3+}$ concentration there are more $\text{Er}^{3+}$ ions available for receiving the excited energy of $\text{Tb}^{3+}$ ions, which reduces the radiative energy of $\text{Tb}^{3+}$ ions.

A close look at the energy level diagrams of $\text{Tb}^{3+}$ and $\text{Er}^{3+}$ shown in Fig. 3 shows that $^4\text{F}_{7/2}$ of $\text{Er}^{3+}$ matches to $^5\text{D}_4$ level of $\text{Tb}^{3+}$. So energy can be easily transferred from $\text{Tb}^{3+}$ to $\text{Er}^{3+}$ as follows.

$\text{Tb}^{3+}$ and $\text{Er}^{3+}$ are randomly distributed in glass matrix. When the glass matrix is excited by 365 nm group of mercury lines, $\text{Tb}^{3+}$ ions rapidly depopulate to luminescent level $^5\text{D}_4$ and $\text{Er}^{3+}$ to ground state $^4\text{I}_{15/2}$. As the decay time of the metastable state $^5\text{D}_4$ of $\text{Tb}^{3+}$ is 2.5 ms, it has enough time to transfer its energy to $^4\text{F}_{7/2}$ of $\text{Er}^{3+}$.

Fig. 1—Emission spectra of (A) $\text{Tb}^{3+}$ (1 wt %) (B) $\text{Tb}^{3+}$ (1 wt %) + $\text{Er}^{3+}$ (0.6 wt %)
The linearity of Fig. 4 shows that electric dipole-dipole interaction is mainly responsible for the energy transfer, which supports the Fong-Diesler theory. The average donor-acceptor distance varies from 1.45 nm to 1.71 nm (Table 1) also in support of electric dipole-dipole interaction suggested by Dexter.

The critical transfer distance at which the probability of energy transfer is equal to radiative decay in present case is equal to 1.59 nm. The critical transfer distance can be compared with the results of

![Figure 4](image1)

**Table 1**—Energy transfer and energy transfer probabilities and donor-acceptor distances between donor (Tb$^{3+}$) and acceptor (Er$^{3+}$)

<table>
<thead>
<tr>
<th>$C_{\text{donor}}$ (wt%)</th>
<th>$C_{\text{acceptor}}$ (wt%)</th>
<th>$D_{\text{D-A}}$ (nm)</th>
<th>$I_d$ (±1)</th>
<th>$I_{do}$ (±1)</th>
<th>$\eta$ (±0.05)</th>
<th>$P_{da} \times 10^2$ S$^{-1}$ (±0.05)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.2</td>
<td>1.71</td>
<td>63</td>
<td>0.30</td>
<td>1.71</td>
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<td></td>
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<td>0.47</td>
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<td>4.57</td>
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<tr>
<td>0.6</td>
<td>1.56</td>
<td></td>
<td>40</td>
<td>0.51</td>
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<tr>
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<td>1.50</td>
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<td>42</td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1.45</td>
<td></td>
<td>36</td>
<td>0.60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$C_{\text{donor}}$ is donor concentration, $C_{\text{acceptor}}$ the acceptor concentration, $D_{\text{D-A}}$ the average donor-acceptor distance, $I_d$ the donor intensity in presence of acceptor, $I_{do}$ the donor intensity in absence of acceptor, $\eta$ the energy transfer efficiency $= \frac{1 - \left( \frac{I_d}{I_{do}} \right)}{\tau}$ and $P_{da}$ the energy transfer probability $= \frac{1}{\tau} \left( \left( \frac{I_{do}}{I_d} \right) - 1 \right)$.

![Figure 2](image2)

![Figure 3](image3)

![Figure 4](image4)
Nakazava and Shionoya\textsuperscript{10} in calcium metaphosphate glass for various rare earth ion pairs lying between 0.3 nm and 1.2 nm, Joshi et al.\textsuperscript{11} (1.91 nm) for Dy\textsuperscript{3+}-Ho\textsuperscript{3+} in zinc phosphate glass and Eyal et al\textsuperscript{12} (2.1 nm) for Mn\textsuperscript{3+}-Tm\textsuperscript{3+} system in metal fluoride for electric dipole-dipole interaction.

Energy transfer by exchange process is negligible in present case because it needs acceptor-donor separation of about 0.3 to 0.4 nm with overlap of wavefunction, while in present case donor acceptor distance varies from 0.95 nm to 1.63 nm.

Since the absorption peak (490 nm) of Er\textsuperscript{3+} ions falls on emission peak (490 nm) of Tb\textsuperscript{3+}, the possibility of small radiative energy transfer from Tb\textsuperscript{3+} to Er\textsuperscript{3+} can’t be ruled out.

4 Conclusions

A non-radiative energy transfer from Tb\textsuperscript{3+} to Er\textsuperscript{3+} in zinc phosphate glass has been observed with transfer efficiency from 0.30 to 0.60. Energy transfer mechanism is mainly found dipole-dipole interaction.

References

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![Absorption spectra Er\textsuperscript{3+} (1 wt %) in zinc phosphate glass](image-url)