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# MULTIPHONON RELAXATION OF RARE EARTH IONS IN BORATE, PHOSPHATE, GERMANATE AND TELLURITE GLASSES*

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Non-radiative multiphonon relaxation rates were obtained for excited electronic states in borate, phosphate, germanate and tellurite glasses. The rates were calculated from the intensities of fluorescence in the visible range of the spectrum, the measured radiative transitions and the decay times of fluorescence. A functional dependence was found between the relaxation rates and the energy gaps of the rare earth ion. It was shown that by changing the glass host from the borate to tellurite matrix, an increase in visible fluorescence was achieved. This was especially notable in $Er^{3+}$, where the increase of fluorescence from germanate to tellurite was by a factor of 15.

## 1. Introduction

When a rare earth ion in a crystal is excited to one of its upper levels, it may decay radiatively by ion–ion interaction or by the emission of several phonons. The problem of the multiphonon orbit–lattice relaxation of excited states of the rare earth ions in crystals has been treated recently (see refs. [1]–[4]). These studies have shown that when the phonon occupation number is smaller than 1 and coupling with the phonons is weak, the internal multiphonon relaxation transition probability, $W_{\mathrm{MRT}}$, can be given by

$$W_{\mathrm{MRT}}(\Delta E) = W_{\mathrm{MRT}}(0)\exp(-\alpha\Delta E)\,, \tag{1}$$

where $W_{\mathrm{MRT}}(0)$ is the transition probability at $\Delta E = 0$, $\Delta E$ is the energy gap between two successive levels, and $\alpha$ is expressed by

$$\alpha = (h\omega)^{-1}\left(\ln\frac{N}{g(n+1)} - 1\right)\,. \tag{2}$$

Here $g$ is the electron–phonon coupling constant, $h\omega$ is the energy of the phonon which contributes predominantly to the relaxation process, $N$ is the number of phonons emitted in the process, namely $N = \Delta E/h\omega$, and $n$ is the phonon occupa-

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tion number. From this it follows that the probability of non-radiative relaxation between two electronic levels decreases with the number of phonons matching the energy gap $\Delta E$, provided that there is no significant change in the value of $g$.

The majority of the works dealing with the multiphonon relaxation are concerned mainly with the effect of temperature on these relaxation probabilities as a function of the energy gap between the electronic levels. Thus far, crystal hosts were investigated. In this work, we studied the effect of the glass matrix on multiphonon relaxation rates. Such a study has practical importance in controlling quantum efficiencies of fluorescence from a given level by choosing the proper glass host. The systems which were studied in this work are $Eu^{3+}$, $Er^{3+}$ and $Tm^{3+}$ doped phosphate, borate, germanate and tellurite glasses.

## 2. Experimental method

The materials and procedure for preparing the phosphate $Na_2O \cdot P_2O_5$ and borate $Na_2O \cdot 2B_2O_3$ glasses are described in refs. [5] and [6], respectively. For preparation of the germanate glass of final composition $17K_2O \cdot 17BaO \cdot 66GeO_2$, see ref. [7] and for that of tellurite glass, $3Na_2O \cdot 7TeO_2$, see ref. [8].

The absorption spectra of glasses were recorded on a Cary 14 spectrophotometer using undoped glass as a blank. The emission and excitation spectra were obtained on the spectrofluorimeter described earlier [9]. The decay times of the fluorescence were measured using this spectrofluorimeter, where the light source was replaced by a flash unit with an EGG-FX-6 AU flash-lamp, having an average pulse duration of 3 μs. The photomultiplier was connected directly to a Tektronix type 502 dual-beam oscilloscope containing a plug-in unit with an attached Polaroid camera. The emissions were measured in the range between 300 and 700 nm. All measurements were made at room temperature.

## 3. Results

The energy levels of the dopant ions $Eu^{3+}$, $Er^{3+}$ and $Tm^{3+}$ are shown in fig. 1.

### 3.1. $Eu^{3+}$

Figure 2 shows part of the emission spectra of $Eu^{3+}$ in various glasses. The transitions appearing in the figure are from $^5D_3$, $^5D_2$ and $^5D_1$ excited levels to the $^7F$ manifold of the ground state. The emission from the $^5D_0$ level to the $^7F$ manifold is by one order of magnitude higher and is not shown in this figure. The assignment of the bands appearing in fig. 2 are given in table 1. As seen in this figure, the transitions from $^5D_3$ and $^5D_2$ to $^7F$ manifold do not appear in borax and phosphate glasses. A notable increase in the emission intensity is observed in the order of bo-

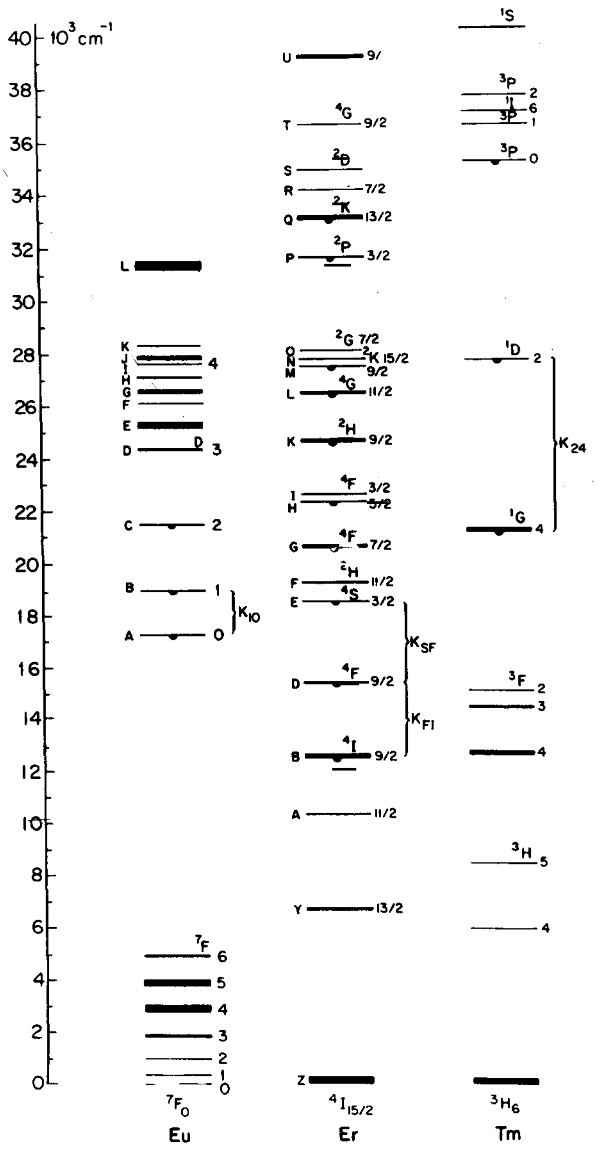

Fig. 1. Energy levels of $Eu^{3+}$, $Er^{3+}$ and $Tm^{3+}$ ions.

rax < germanate < tellurite. The relative areas under the fluorescence curves of $^5D_1$ and $^5D_0$ are given in table 2.

The decay times of the fluorescence from the $^5D_0$ level of $Eu^{3+}$ were simple exponentials in all glasses. Their values are 2.83 ms in phosphate, 1.7 ms in germanate and 1.01 ms in tellurite.

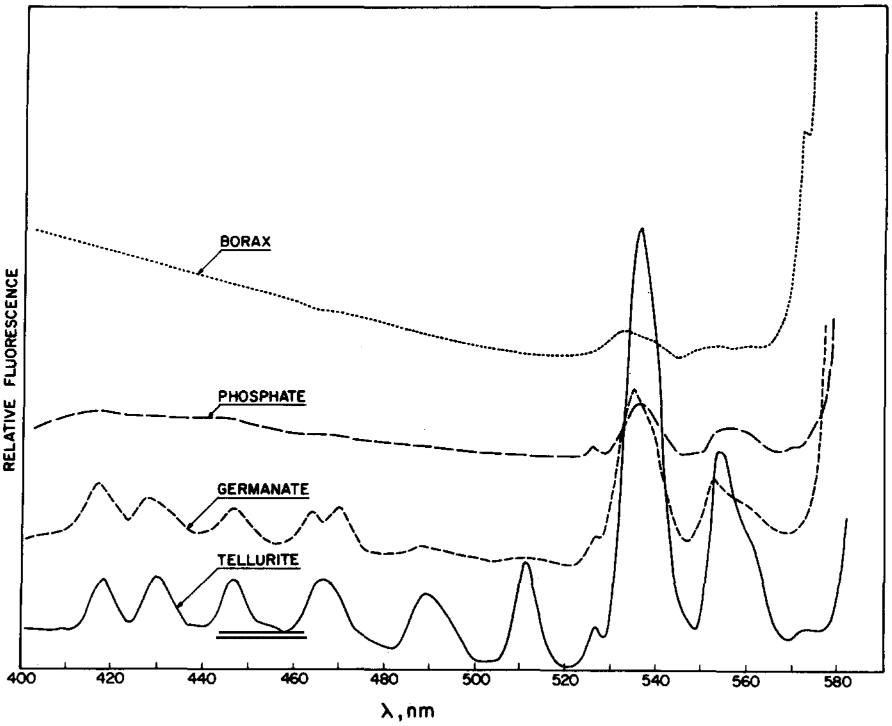

Fig. 2. Part of the emission spectra of $Eu^{3+}$ in various glasses.

The transition probability $K_{10}$ from state $^5D_1$ to $^5D_0$ of $Eu^{3+}$ was calculated using the following rate equations for depopulation of the system.

$$dN_1/dt = -(k_{10} + k_{1g})N_1 , \tag{3}$$

$$dN_0/dt = k_{10}N_1 - (k_{0g}^{r} + k_{0g}^{nr})N_0 . \tag{4}$$

The symbols in these equations have the following meanings: $k_{1g}$ – total transition probability from the $^5D_1$ level to the $^7F$ ground multiplet; $k_{0g}$ – transition probability from the $^5D_0$ level to the $^7F$ multiplet; r and nr – radiative and non-radiative transitions respectively; $N_1$ and $N_0$ – the population of the levels $^5D_1$ and $^5D_0$ at a given time; $k_{0g}^{nr} \to 0$ because of the high energy gap between the $^5D_0$ and $^7F$ levels. Assigning by $J$ the integral $\int N_j(t)\,dt$ we have

$$J_0 = \int_0^\infty N_0(t)\,dt , \tag{5a}$$

Table 1
Assignments of the observed fluorescence bands of $Eu^{3+}$. [a]

| Band (nm) | Assignment |
|---|---|
| 416 | $^5D_3 \rightarrow {}^7F_0$ |
| 430, 448 | not defined |
| 464 | $^5D_2 \rightarrow {}^7F_0$ |
| 470 | $^5D_2 \rightarrow {}^7F_1$ |
| 490 | $^5D_2 \rightarrow {}^7F_2$ |
| 510 | $^5D_2 \rightarrow {}^7F_3$ |
| 527 | $^5D_1 \rightarrow {}^7F_0$ |
| 536 | $^5D_1 \rightarrow {}^7F_1$ |
| 555 | $^5D_1 \rightarrow {}^7F_2$ |

[a] The transitions from $^5D_0$ are not shown.

Table 2
Relative areas of the emission of $Eu^{3+}$ in various glasses.

| Transition | Borate | Phosphate | Germanate | Tellurite |
|---|---|---|---|---|
| $^5D_0 \rightarrow {}^7F_0$ | 100 | 100 | 100 | 100 |
| $^5D_1 \rightarrow {}^7F_2$ | – | 14.5 | 24.9 | 82.3 |
| $^5D_1 \rightarrow {}^7F_1$ | 2.5 | 21.3 | 35.0 | 176.2 |
| $^5D_1 \rightarrow {}^7F_0$ | 0.9 | 2.0 | 0.7 | 3.8 |

$$J_1 = \int_0^\infty N_1(t)\,dt\,. \tag{5b}$$

The time integrated luminescence intensity of a state $|j\rangle, \mathcal{I} \equiv \int I\,dt$, of the system is then given by

$$\mathcal{I}_j = K_j^r J_j \tag{6}$$

which holds for continuous irradiation. $K_j^r$ is the radiative transition probability from the $j$th level ($^5D_1$ or $^5D_0$) to the ground $^7F$ multiplet.

Integration of eqs. (3) and (4) and using eq. (5) gives

$$-N_1(0) = -(k_{10} + k_{1g})J_1\,, \tag{7}$$

$$-N_0(0) = k_{10}J_1 - k_{0g}^r J_0\,. \tag{8}$$

If the absorption is into level $|^5D_1\rangle$ then $N_0(0) = 0$.

$$k_{10}J_1 = k_{0g}^r J_0\,. \tag{9}$$

From eq. (6),

$$J_1 = \mathcal{I}_1/k^{\mathrm{r}}_{1\mathrm{g}} \quad \text{and} \quad J_0 = \mathcal{I}_0/k^{\mathrm{r}}_{0\mathrm{g}} .$$

Then eq. (9) becomes

$$k_{10}\ (\mathcal{I}_1/k^{\mathrm{r}}_{1\mathrm{g}}) = \mathcal{I}_0 , \tag{10}$$

from which it follows that

$$k_{10} = (\mathcal{I}_0/\mathcal{I}_1)\ k^{\mathrm{r}}_{1\mathrm{g}} . \tag{11}$$

The numerical value of $k^{\mathrm{r}}_{1\mathrm{g}}$ can be calculated from the transition probability ${}^7\mathrm{F}_0 \to {}^5\mathrm{D}_1$ which was obtained from absorption and the relative areas (5) of all the transitions ${}^5\mathrm{D}_1 \to {}^7\mathrm{F}_i$

$$k^{\mathrm{r}}_{1\mathrm{g}} = \frac{1}{\Sigma\tau_{\mathrm{nat}}} = k({}^5\mathrm{D}_1 \to {}^7\mathrm{F}_0)\left(1 + \frac{\Sigma_{i=1}^{6} S({}^5\mathrm{D}_1 \to {}^7\mathrm{F}_i)}{S({}^5\mathrm{D}_1 \to {}^7\mathrm{F}_0)}\right) , \tag{12}$$

where $S$ is the area under the relevant transition. It is assumed in eq. (12) that $k({}^7\mathrm{F}_0 \to {}^5\mathrm{D}_1) = k({}^5\mathrm{D}_1 \to {}^7\mathrm{F}_0)$. The value $1/\tau_{\mathrm{nat}} = k({}^7\mathrm{F}_0 \to {}^5\mathrm{D}_1)$ is taken from formula (13), which is valid for the narrow level system [10]

$$1/\tau_{\mathrm{nat}} = 2.88 \times 10^{-9} n^2 (gl/gu) \langle\nu\rangle^2 \int \epsilon(\nu)\mathrm{d}\nu , \tag{13}$$

where $n$ is the refraction index, $\langle\nu\rangle^2$ the squared average wave number of the absorption, $gl$, $gu$ the degeneracies of the lower and upper states, $\epsilon(\nu)$ the extinction coefficient as a function of the wave number.

The values of $k^{\mathrm{r}}_{1\mathrm{g}}$ were calculated using eq. (12) in which only three transitions ${}^5\mathrm{D}_1 \to {}^7\mathrm{F}_{0,1,2}$ were included. Other transitions were hidden under the emission bands of the ${}^5\mathrm{D}_0 \to {}^7\mathrm{F}$ multiplet.

The values so obtained for $k^{\mathrm{r}}_{1\mathrm{g}}$ were 53.7 $\mathrm{s}^{-1}$ in phosphate, 70.48 $\mathrm{s}^{-1}$ in germanate and 57.05 $\mathrm{s}^{-1}$ in tellurite. From these, the transition probabilities $k_{10}$ were obtained: 1.57 $10^4$ $\mathrm{s}^{-1}$, 7.05 $10^3$ $\mathrm{s}^{-1}$ and 3.98 $10^3$ $\mathrm{s}^{-1}$ for phosphate, germanate and tellurite respectively.

Weber [11] in this work on $\mathrm{Eu}^{3+}$ doped $\mathrm{LaF}_3$, calculated the radiative probabilities for all the transitions from the ${}^5\mathrm{D}_1$ to ${}^7\mathrm{F}$ multiplet and obtained the ratio

$$k({}^5\mathrm{D}_1 \to {}^7\mathrm{F}_{0,1,2,3,4,5,6})/k({}^5\mathrm{D}_1 \to {}^7\mathrm{F}_{0,1,2}) = 130/80 .$$

It is expected that a similar ratio will be obtained in the case of glasses. Therefore, the actual value of $k^{\mathrm{r}}_{1\mathrm{g}}$ should be greater by such a factor, increasing correspondingly the value of $k_{10}$.

### 3.2. $Tm^{3+}$

The electronic transitions $^1G_4 \rightarrow {}^3H_4$ (~652 nm) and $^3F_2 \rightarrow {}^3H_6$ (~670 nm) of $Tm^{3+}$ in various glasses are shown in fig. 3. The excitation was to the $^1G_4$ level and the emission spectra were corrected for the absorption of this level in the different media. Thus, this figure shows the relative quantum efficiencies. It is evident from the figure that the emission intensities increase in order similar to that observed in $Eu^{3+}$. Using the experimentally obtained emission intensities from the $^1G_4$ level and the absorption coefficients, the probability of relaxation from the higher $^1D_2$ level to the next lower level $^1G_4$ was calculated. The rate equations for such cases are similar to those developed by Nakazawa and Shionoya [12] and the present authors for depopulation of $^1D_2$ to $^1G_4$ emitting levels of $Tm^{3+}$ [13]. The final equation used for calculation of the relaxation rate $K_{24}$ from $^1D_2$ to $^1G_4$ is

$$K_{24} = (I_{24}J_4/I_{44}J_2)(B_4/B_2)(1/\tau_2)\,. \tag{14}$$

Here $I$ represents the emission intensities, and the suffixes 2 and 4 mean the levels $^1D_2$ and $^1G_4$, the first suffix indicating the level excited and the second one the emitting level. $B$ and $J$ denote the absorption cross-section and the exciting photon

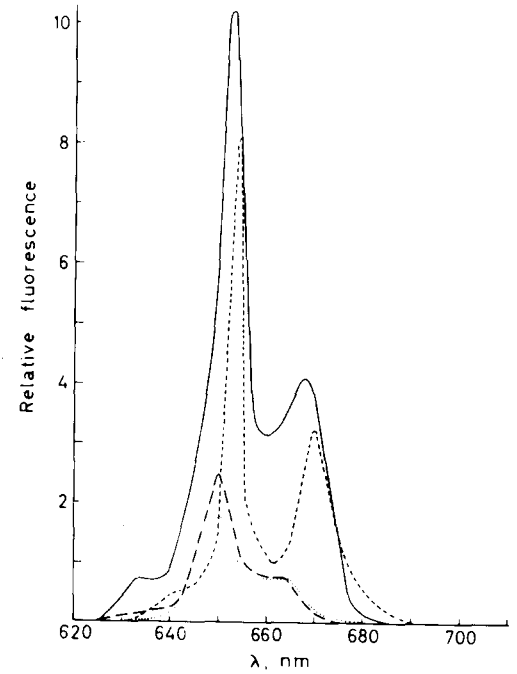

Fig. 3. Emission spectra of $Tm^{3+}$ in various glasses normalized for the absorption. Excited at $^1G_4$ (469 nm). —— tellurite; - - - - - germanate; — — — phosphate; · · · · · borate.

flux respectively. $\tau_2$ is the measured lifetime of the $^1D_2$ level. The values of $K_{24}$ thus obtained for various glasses are shown in fig. 4.

### 3.3. $Er^{3+}$

Figure 5 shows the relative spectral efficiencies of the $^2H_{9/2} \rightarrow {}^4I_{15/2}$ (~408 nm), $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (~525 nm), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (~535, 546 and 556 nm) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (~660 nm) transitions of $Er^{3+}$ in germanate and tellurite glasses. The spectra shown in this figure are corrected for the absorption of the $^4G_{11/2}$ (~380 nm) excited level in the two different media and corrected for the spectral distribution of the light source, response of the photomultiplier and monochromators.

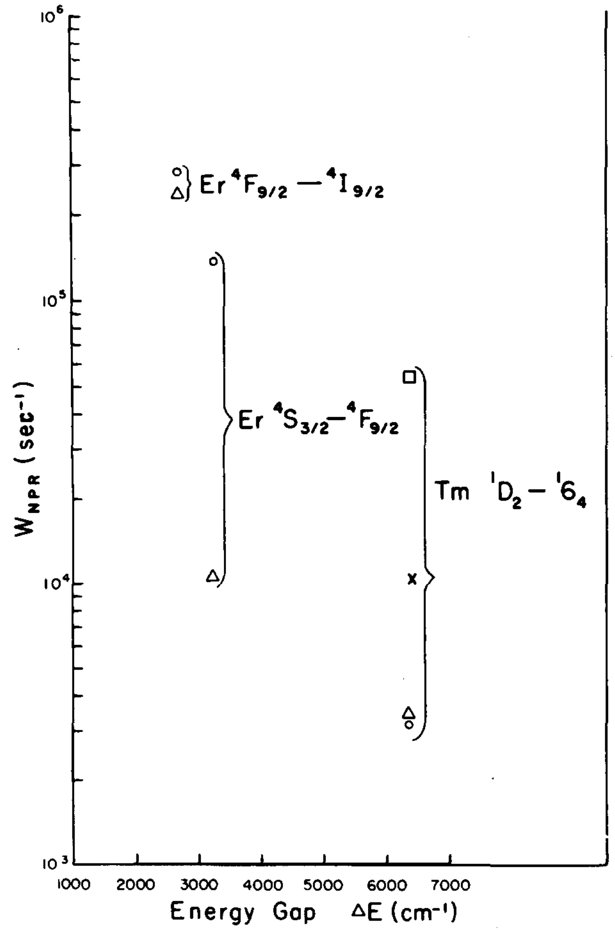

Fig. 4. Multiphonon relaxation rates of rare earth ions, in different glasses, as a function of the energy gaps. ○ germanate; × phosphate; △ tellurite; □ borate.

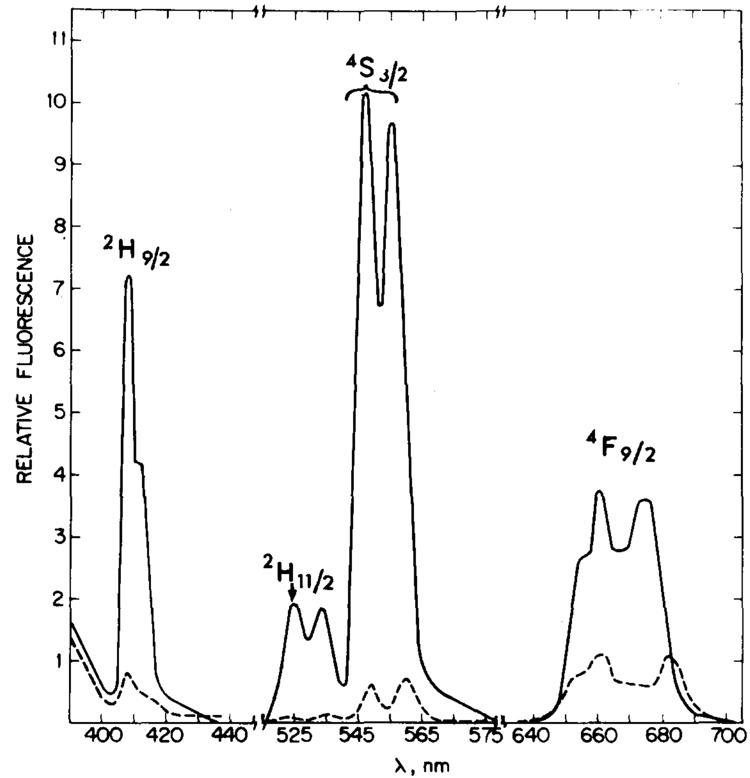

Fig. 5. The emission spectrum of $Er^{3+}$ in germanate and tellurite glasses normalized for the absorption. Excited at $^4G_{11/2}$ (379 nm). ——— tellurite; - - - - - germanate.

As seen, the fluorescent quantum efficiency in tellurite is much higher than in germanate glass. No fluorescence was observed for $Er^{3+}$ doped borate glass and only very weak fluorescence was obtained for $Er^{3+}$ in phosphate glass. The relaxation rates from $^4S_{3/2}$ to $^4F_{9/2}$ ($K_{SF}$) and from $^4F_{9/2}$ to $^4I_{9/2}$ ($K_{FI}$) were calculated by the method described earlier for $Tm^{3+}$. These rates are also shown in fig. 4.

## 4. Discussion

From formula (1), it follows that the probability of non-radiative relaxation between two successive electronic levels decreases with the number of phonons matching the energy gap $\Delta E$.

It was proposed earlier [14] that in oxide glasses, a rare earth ion is surrounded by eight non-bridging oxygens belonging to the corners of $XO_4$ (X = B, P, Ge) glass forming tetrahedra or octahedra of $TeO_2$, each polyhedron donating two oxygens.

Table 3
Phonon energies of various oxidic glasses

| Glass | Bond | Phonon energy ($cm^{-1}$) |
|---|---|---|
| Borate | B–O | 1340–1480 |
| Phosphate | P–O | 1200–1350 |
| Germanate | Ge–O | 975–800 |
| Tellurite | Te–O | 750–600 |

As a result, a distorted cube is formed surrounding the rare earth ion.

In rare earth doped glasses there are two main groups of phonons: the high-energy phonons arising from the X–O stretching frequencies and the low-energy phonons arising from the Me–O bond (Me = $RE^{3+}$, $Na^+$, $K^+$, etc.) In general, the highest energy phonons make the dominant contribution to the non-radiative relaxation, as the multiphonon relaxations occur by emitting the smallest number of phonons which match the energy gap between two successive electronic levels. Therefore, the X–O stretching frequencies with energies, as given in table 3, are mainly responsible for the phonon-assisted relaxation in glasses. The low-energy phonons will become effective if the gap is not exactly matched by the higher energy phonons. From our experimental results we have concluded that the variation in $g$ in various glasses would not explain the observed enhancement in the emission intensities.

The relation between the radiative and non-radiative probabilities and quantum efficiencies $\phi$ of fluorescence is given by

$$\phi = \Sigma K_i^r/(\Sigma K_i^r + \Sigma K_i^{nr}) , \tag{15}$$

where $k^r = \Sigma K_i^r$ represents the radiative and $k^{nr} = \Sigma K_i^{nr}$ the non-radiative transition rates. As seen from formula (15), a decrease in the non-radiative probabilities in cases where the radiative constants are similar results in a higher quantum efficiency, which is governed by the energies of the phonons of the host matrix [2].

In $Eu^{3+}$, the energy gaps between the metastable levels from which fluorescence may be observed are

$$^5D_0 \to {}^7F_0 \approx 17\,000\ cm^{-1} ,\ {}^5D_1 \to {}^5D_0 \approx 1650\ cm^{-1} ,$$

$$^5D_2 \to {}^5D_0 \approx 2600\ cm^{-1} .$$

In phosphate and borate glasses, where one phonon of X–O bond is needed for the matching of the energy gap between $^5D_1 \to {}^5D_0$, the non-radiative rate is high and the fluorescence from the $^5D_1$ level is very low. In germanate and tellurite glasses, the energy gap can be matched by two to three X–O phonons and fluorescence from $^5D_1$ and even $^5D_2$ is observed with high intensity.

In erbium, the energy gaps between two close-lying electronic levels are about 1000–3000 $\mathrm{cm}^{-1}$. As a consequence of the small energy gaps combined with the high phonon energies of borate and phosphate, rapid non-radiative depopulation of the erbium levels situated between 32 000 and 10 000 $\mathrm{cm}^{-1}$ occurs, resulting in very low intensity emission. In germanate and tellurite, which have smaller phonon energies than borate and phosphate, the non-radiative losses are smaller and intense fluorescence from $^2H_{9/2}$, $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ is observed.

In thulium, as in erbium, the emission intensities are highest in the tellurite glasses. The energy gaps between the various electronic levels of thulium situated between 35 000 and 15 000 $\mathrm{cm}^{-1}$ are about 6000 $\mathrm{cm}^{-1}$, which correspond to the energy of 4 phonons in borate, about 5 in phosphate, 7 in germanate and 9–10 in tellurite glasses. Hence the observed fluorescence is the highest in tellurite.

From our experimental results, we see that the dependence of emission intensities on the phonon energies is stronger when the energy gap $\Delta E$ between the emitting levels is smaller. For example, in the case of emission from Er $^4S_{3/2}$ ($\Delta E$ ($^4S_{3/2}$ – $^4F_{9/2}$) ~ 2650 $\mathrm{cm}^{-1}$), the fluorescence is higher by a factor of 15 in the tellurite than in the germanate glass, while in the case of emission from Tm $^1G_4$ ($\Delta E$ ($^1G_4$ – $^3F_2$) ~ 6000 $\mathrm{cm}^{-1}$), the ratio of fluorescence in tellurite to germanate is only 1.3.

The numerical values of non-radiative rate constants differ much less than the values of quantum efficiencies in various glasses. As seen in formula (15), the quantum efficiency depends on both the non-radiative and the radiative transition rates. Therefore, the increase in the quantum efficiency is not always followed by a similar increase in the multiphonon relaxation rate.

In summary, we can see that by incorporating the activator ion in the glass host of a proper phonon energy it is possible to increase the quantum efficiency of emission and control the levels from which emission occurs.

## Acknowledgement

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