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## Effect of cross relaxation on the 1470 and 1800 nm emissions in $\text{Tm}^{3+}:\text{TeO}_2\text{-CdCl}_2$ glass

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### Abstract

We have used spectroscopic methods to investigate the effect of cross relaxation on the 1470 and 1800 nm emissions in  $\text{Tm}^{3+}:\text{TeO}_2\text{-CdCl}_2$  glass for  $\text{Tm}^{3+}$  ion concentrations of 0.05, 0.1, 0.25, 0.5 and 1.0 mol%. The emission spectra obtained under 800 nm excitation reveal the existence of energy transfer via cross relaxation among the  $\text{Tm}^{3+}$  ions. As a result, as the thulium concentration is increased, the strength of the 1470 nm emission is found to decrease in relation to that of the 1800 nm emission. The analysis of the time evolution of the  $^3\text{F}_4$  emission due to the  $^3\text{F}_4 \rightarrow ^3\text{H}_6$  transition further shows that the electronic mechanism responsible for the ion–ion interaction can be identified as an electric dipole–dipole energy transfer process and occurs in the diffusion-limited relaxation regime. The average critical distance parameter which provides a measure for the strength of cross relaxation was further determined to be 17.9 Å.

### 1. Introduction

$\text{Tm}^{3+}$ -doped glasses possess several favourable spectroscopic characteristics that make them attractive for important technological applications in the near infrared. When pumped around 800 nm, the  $\text{Tm}^{3+}$  ion emits in two broad bands centred at 1470 and 1800 nm, following excitation from the ground state  $^3\text{H}_6$  to the upper state  $^3\text{F}_4$ . The 1470 nm emission is potentially important in the development of fibre-optic amplifiers that can extend the gain bandwidth of the present-day systems based on  $\text{Er}^{3+}$ -doped fibres [1]. In addition, the 1800 nm emission is suitable for the construction of  $\text{Tm}^{3+}$ -based fibre laser systems for medical as well as for spectroscopic applications.

Two important factors that influence the quantum efficiency of the luminescence bands are the glass host and the active ion concentration. Typically, hosts with good thermal and chemical stability and high refractive index are desirable. Among the existing alternatives, tellurite-based glasses offer several advantages due to their chemical stability, wide transparency window in

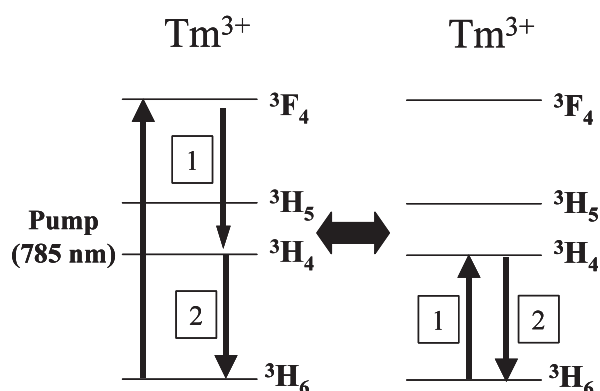
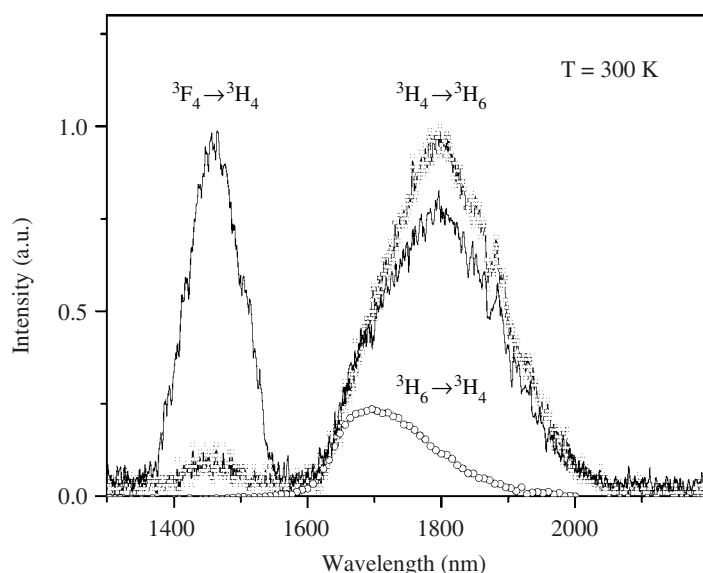


Figure 1. Energy-level diagram of two thulium ions showing the process of cross relaxation.

the infrared, ease of incorporating rare-earth ions into the lattice and high refractive index. Furthermore, the lattice phonon energies are lower than common oxide glass formers such as silicates and borates. This reduces the strength of non-radiative decay from the metastable levels and increases the luminescence quantum efficiency [2]. The glass composition needs to be further optimized in order to maximize the emission strengths of the bands. In previous studies, we investigated the dependence of the infrared luminescence efficiencies as a function of the  $\text{CdCl}_2$  fraction in tellurite-based glasses with the composition of  $(1-x)\text{TeO}_2+(x)\text{CdCl}_2$ , and found that emission cross sections were highest for samples with 30 mol%  $\text{CdCl}_2$  [3].

The second important factor that affects the strength of the luminescence bands is the active ion concentration. Typically, as the concentration of  $\text{Tm}^{3+}$  ions is increased, the relative strength of the luminescence bands may vary due to cross relaxation. The energy transfer mechanism during this process is schematically shown in figure 1. When the concentration is sufficiently high, a  $\text{Tm}^{3+}$  ion decaying from state  $^3\text{F}_4$  to  $^3\text{H}_{4,5}$  induces a second  $\text{Tm}^{3+}$  ion in its ground state to be promoted to the energy level  $^3\text{H}_4$  via predominantly electric dipole–dipole interaction (arrows labelled 1). This results in the emission of two photons in the infrared for one pump photon (arrows labelled 2) and can lead to a reduction in the efficiency of the 1470 nm band in relation to the 1800 nm emission. In the development of thulium-based glasses for amplifier and laser applications, it is therefore very important to determine the range of active ion concentrations where cross relaxation acts as the dominant energy transfer mechanism.

In this study, we have used spectroscopic methods to investigate the effect of cross relaxation on the 1470 and 1800 nm emissions in  $\text{Tm}^{3+}:\text{TeO}_2\text{-CdCl}_2$  glass. Samples with five different thulium concentrations were prepared and characterized by measuring the relative strengths of the emission bands. Fluorescence decay measurements were also carried out to determine the lifetimes of the  $^3\text{H}_4$  and  $^3\text{F}_4$  levels as a function of the  $\text{Tm}^{3+}$  ion concentration. The Judd–Ofelt analysis was then used to determine the luminescence quantum efficiency of each transition at different concentrations. Results show that at the thulium concentration of around 0.1 mol%, the integrated strengths of these emission bands are nearly equal. As the thulium concentration is increased, the strength of the 1470 nm emission decreases in relation to the 1800 nm emission because of cross relaxation. The luminescence quantum efficiencies were also found to decrease with increasing ion concentration. Finally, the average critical distance parameter, which provides a measure of the strength of cross relaxation, was estimated to be 17.9 Å in the diffusion-limited relaxation regime.



**Figure 2.** Luminescence spectra of the  $\text{Tm}^{3+}:\text{0.7TeO}_2:\text{0.3CdCl}_2$  samples with 0.1 mol% (solid curve) and 1.0 mol% (open squares) thulium concentrations in the near infrared wavelength region. The absorption band (open circles) of the  ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$  transition is also included to show that the spectral overlap with the 1470 nm emission is very small.

## 2. Experimental details

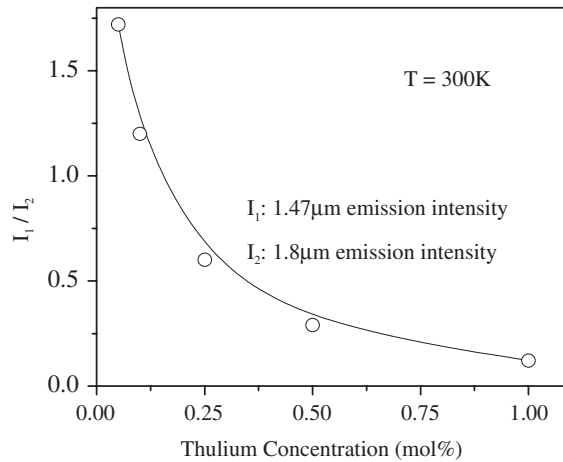
A detailed description of sample preparation and characterization methods can be found in [3]. Briefly, thulium-doped tellurite glasses with the composition  $x\text{Tm}:\text{0.7TeO}_2:\text{0.3CdCl}_2$  were prepared with  $x = 0.05, 0.1, 0.25, 0.5$  and 1 mol%. Each sample with a batch size of 7 g was heated in a platinum crucible at  $750^\circ\text{C}$  for 30 min and rapidly quenched by pressing between graphite slabs.

The absorption spectra of the polished samples were recorded with a spectrophotometer (Shimadzu UV-VIS-NIR 3101 PC) in the 300–2000 nm wavelength range. The integrated absorption coefficient of each band was calculated to determine the thulium concentration in different samples. It was found that the absorption coefficient has a linear dependence on the  $\text{Tm}^{3+}$  ion concentration. This indicates that the thulium concentrations are in agreement with the nominal values.

Luminescence measurements were made with a 0.5 m Czerny–Turner-type monochromator by exciting the samples with a 785 nm diode. The signal was detected with a PbS photoconductive cell and amplified in two stages by a preamplifier and a lock-in amplifier. In fluorescence lifetime measurements, a home-built pulsed Ti:sapphire laser outputting 70 ns pulses at a pulse repetition rate of 500 Hz or 1 kHz was used. A fast InGaAs detector was used to measure the fluorescence decay signal at 1800 nm to determine the lifetime of the  ${}^3\text{H}_4$  level. The lifetime of the  ${}^3\text{F}_4$  level was further determined by measuring the fluorescence lifetimes at 810 nm with a photomultiplier tube.

## 3. Results and discussion

Figure 2 shows the spectra obtained for 0.1 and 1.0 mol%  $\text{Tm}^{3+}$  ion concentrations. The two emission bands observed are centred at about 1470 and 1800 nm and are due to the  ${}^3\text{F}_4 \rightarrow {}^3\text{H}_4$



**Figure 3.** Ratio of the integrated luminescence intensity of the  ${}^3F_4 \rightarrow {}^3H_4$  transition ( $I_1$ ) to that of the  ${}^3H_4 \rightarrow {}^3H_6$  transition ( $I_2$ ).

and  ${}^3H_4 \rightarrow {}^3H_6$  transitions, respectively. The width (FWHM) and the peak wavelength of both luminescence bands do not change with  $Tm^{3+}$  concentration. However, the ratio of the integrated luminescence intensity of the transition  ${}^3F_4 \rightarrow {}^3H_4$  to that of the  ${}^3H_4 \rightarrow {}^3H_6$  transition decreases with increasing  $Tm^{3+}$  concentration as shown in figure 3. For example, the ratio was measured to be 1.75 and 0.16 for  $Tm^{3+}$  concentrations of 0.05 and 1.0 mol%, respectively.

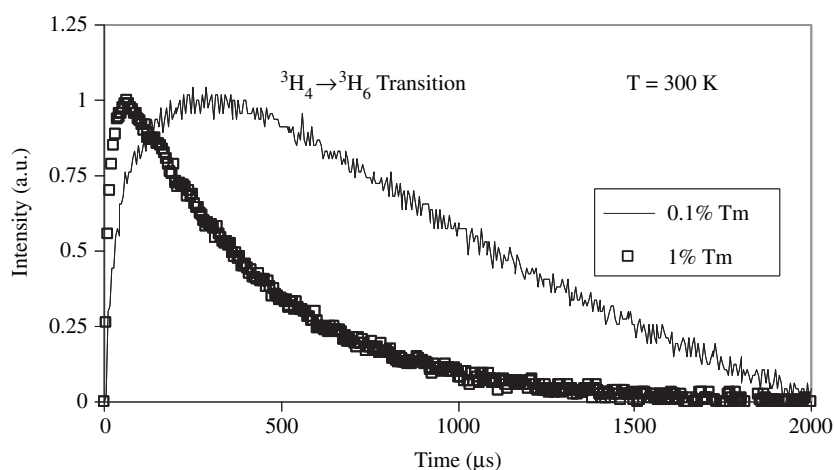
The variation in the relative intensities of the 1470 and 1800 nm bands can occur as a result of three possible processes: (i) relaxation by multi-phonon emission to the  ${}^3H_4$  and  ${}^3H_5$  levels, (ii) cross relaxation between  $Tm^{3+}$  ion pairs that populate either the  ${}^3H_5$  or  ${}^3H_4$  level (see figure 1), and (iii) energy migration to quenching sites. The last two processes depend on the thulium concentration in the host. The  ${}^3H_4$  level of thulium may be populated via only processes (i) and (ii) after the excitation of the  ${}^3F_4$  level. The energy difference between the  ${}^3F_4$  and  ${}^3H_5$  levels is  $4344\text{ cm}^{-1}$  and the energy of the highest phonon in tellurite glasses is about  $780\text{ cm}^{-1}$  [4]. This means that at least six phonons are needed, suggesting that this multi-phonon process is weak and can be neglected in the present case.

The second non-radiative channel to be considered is cross relaxation of the  ${}^3F_4$  level via the  $[{}^3F_4, {}^3H_6] \rightarrow [{}^3H_{4,5}, {}^3H_4]$  process. Luminescence centred at 1470 nm originates from the  ${}^3F_4$  level and suffers from this cross-relaxation process. As a result, the population of the lower level of the 1470 nm transition increases and reduces the population inversion between the  ${}^3F_4$  and the  ${}^3H_4$  levels. This difficulty may be overcome by employing a method such as co-lasing with the 1800 nm emission [5, 6]. Figure 2 also shows that there is almost no spectral overlap between the  ${}^3F_4 \rightarrow {}^3H_4$  emission and  ${}^3H_6 \rightarrow {}^3H_4$  (open circles) absorption bands. Since the energy mismatch between the peak wavelengths of these bands is about  $800\text{ cm}^{-1}$ , this indicates that the cross-relaxation process requires the assistance of phonons.

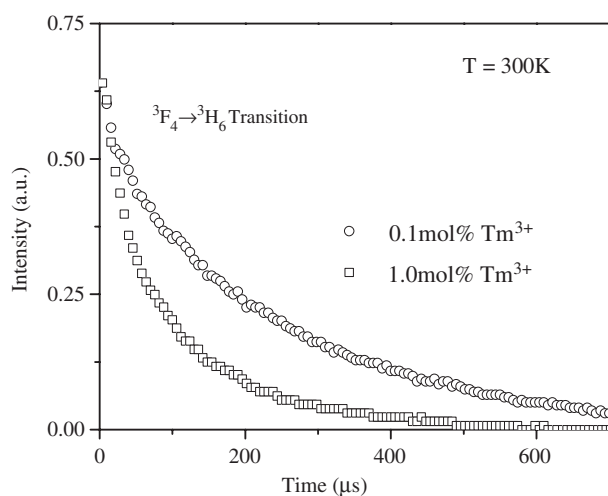
Following the above discussion, the overall decay rate  $W_M$  of the excited state population can be expressed as

$$W_M = W_R + W_{NR} + W_E, \quad (1)$$

where  $W_R$  ( $W_R = 1/\tau_R$ ,  $\tau_R$  = radiative lifetime) is the intrinsic radiative decay rate,  $W_{NR}$  is the non-radiative decay rate due to multi-phonon loss and  $W_E$  is an additional non-radiative decay rate due to the energy transfer processes between the rare earth ions.  $W_M$  corresponds to the

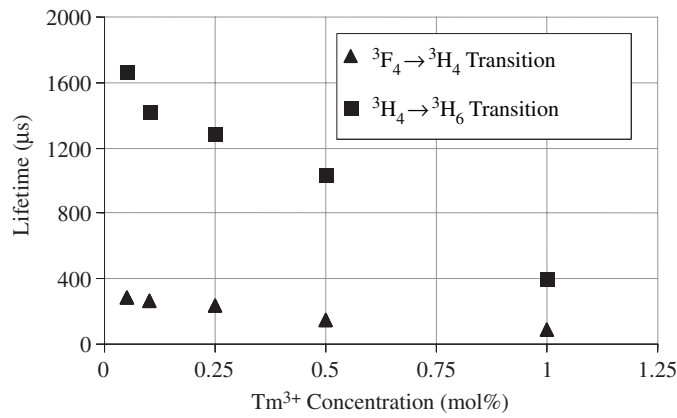


**Figure 4.** Measured decay of the 1800 nm emission in  $\text{Tm}^{3+}:\text{0.7TeO}_2:\text{0.3CdCl}_2$  glass doped with 0.1 mol% (solid curve) and 1.0 mol% (open squares) thulium ions. Excitation was into the  $^3\text{F}_4$  level.



**Figure 5.** Measured decay of the 1470 nm emission in  $\text{Tm}^{3+}:\text{0.7TeO}_2:\text{0.3CdCl}_2$  glass doped with 0.1 mol% (open circles) and 1.0 mol% (open squares) thulium ions. Excitation was into the  $^3\text{F}_4$  level.

fluorescence decay rate which can be determined by measuring the lifetime  $\tau_F$  of the  $^3\text{F}_4$  and  $^3\text{H}_4$  levels. In the experiments,  $\tau_F$  was measured as a function of the  $\text{Tm}^{3+}$  ion concentration. Note that  $W_M = 1/\tau_F$ . Figures 4 and 5 show the time-dependent fluorescence decay curves of the  $^3\text{H}_4$  and  $^3\text{F}_4$  levels, respectively, for samples with 0.1 and 1 mol%  $\text{Tm}^{3+}$ . All the curves of 1800 nm luminescence ( $^3\text{H}_4 \rightarrow ^3\text{H}_6$  transition) show an initial rise, followed by an exponential decay (see figure 4). This is due to the non-negligible lifetime of the  $^3\text{F}_4$  level. The lifetimes were determined by fitting the tail of the decay curve to a single exponential. In the case of the  $^3\text{F}_4$  level (figure 5), the time-dependent fluorescence intensity shows a monotonic non-exponential decay at early times after the pump excitation. The lifetime of this level was determined in a similar way by fitting the tail of the decay curve to a single



**Figure 6.** Measured variation of the decay lifetime  $\tau_F$  of the  ${}^3F_4$  (solid triangles, 1470 nm emission) and  ${}^3H_4$  (solid squares, 1800 nm emission) levels as a function of the thulium concentration for  $Tm^{3+}:0.7TeO_2:0.3CdCl_2$  glass.

**Table 1.** Luminescence lifetimes ( $\tau_F$ ), cross-relaxation rates ( $W_E = 1/\tau_F - 1/\tau_R$ ) and the luminescence quantum efficiencies ( $\eta = \tau_F/\tau_R$ ) for the energy levels  ${}^3F_4$  and  ${}^3H_4$  at different  $Tm^{3+}$  ion concentrations.  $\tau_F$  was measured and  $\tau_R$  was determined from Judd–Ofelt theory. The radiative lifetimes of  ${}^3F_4$  and  ${}^3H_4$  levels were calculated to be 832 and 2540  $\mu s$ , respectively [3].

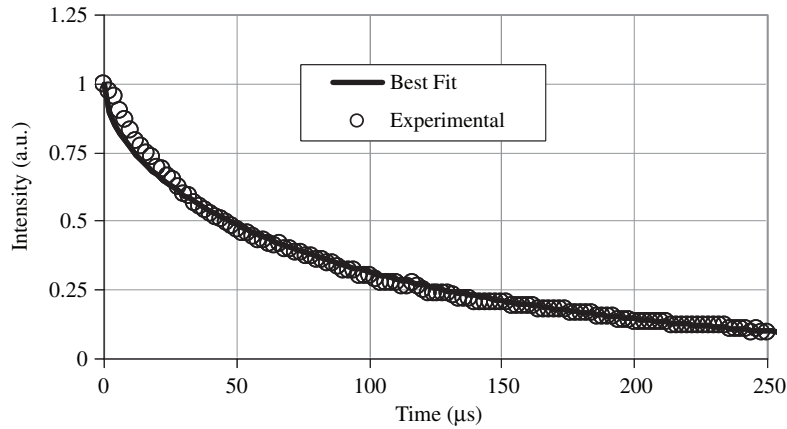
$Tm^{3+}$ concentration (mol%)	$\tau_F$ ( $\mu s$ ) ${}^3F_4$	$\tau_F$ ( $\mu s$ ) ${}^3H_4$	$W_E$ ( $10^{-3} \mu s^{-1}$ ) ${}^3F_4$	$W_E$ ( $10^{-3} \mu s^{-1}$ ) ${}^3H_4$	$\eta$ ${}^3F_4$	$\eta$ ${}^3H_4$
0.05	282	1670	2.3	0.205	0.34	0.66
0.1	262	1420	2.6	0.31	0.31	0.56
0.25	234	1280	3.1	0.39	0.28	0.50
0.5	145	1040	5.7	0.57	0.17	0.41
1.0	86	405	10.4	2.1	0.10	0.16

exponential. The results for both levels are given in table 1 and figure 6 for different  $Tm^{3+}$  ion concentrations. Table 1 also presents the luminescence quantum efficiency  $\eta$  ( $\eta = \tau_F/\tau_R$ ) of these levels at different concentrations. Here, the intrinsic radiative decay rate  $W_E$  was determined from Judd–Ofelt theory [3]. For completeness, the radiative lifetimes determined in [3] are also included in the caption of table 1. Note that  $\eta$  monotonically decreases as a function of concentration. Furthermore, the relative luminescence intensity of the 1800 nm emission increases while its lifetime becomes shorter with increasing  $Tm^{3+}$  concentration. On the other hand, both the intensity and the lifetime of the 1470 nm luminescence decrease when the  $Tm^{3+}$  concentration is increased as expected. A possible explanation for the decrease of the 1800 nm fluorescence lifetime is energy migration between thulium ions in the  ${}^3H_4$  level.

Energy transfer processes such as cross relaxation, are generally described in terms of three limiting cases: (i) direct relaxation, (ii) fast diffusion and (iii) diffusion limited relaxation [7]. Fast diffusion is characterized by a simple exponential behaviour. The population,  $N(t)$ , of the metastable donor level from which the luminescence originates can be expressed as a function of time as

$$N(t) = \exp[-t/\tau_R - \Pi(t)], \quad (2)$$

where  $\tau_R$  is the radiative lifetime of the emitting level. The second term  $\Pi(t)$ , includes the information about the nature of the energy transfer processes. For the case where one type of active ion is present in the host, neighbouring ions around the excited ion can behave either



**Figure 7.** Measured and calculated decay of the  ${}^3F_4 \rightarrow {}^3H_4$  transition for the Tm<sup>3+</sup>:0.7TeO<sub>2</sub>:0.3CdCl<sub>2</sub> glass sample containing 0.5 mol% Tm<sup>3+</sup> ions. The solid curve is the best fit to equation (3). The best-fit values of  $C$ ,  $D$  and  $R_0$  were determined to be  $0.515 \times 10^{-38} \text{ cm}^6 \text{ s}^{-1}$ ,  $2.44 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  and  $12.7 \text{ \AA}$ , respectively.

as acceptors or as centres for the energy migration. Hence, in our case, cross relaxation among Tm<sup>3+</sup> ions can be described by a diffusion-limited relaxation mechanism as discussed by Yokota and Tanimoto [8]. In this limit,  $N(t)$  becomes

$$N(t) = \exp \left[ -t/\tau_R - \frac{4}{3} \pi^{3/2} N_A C^{1/2} t^{1/2} \left( \frac{1 + 10.87x + 15.50x^2}{1 + 8.743x} \right)^{3/4} \right], \quad (3)$$

where  $N_A$  is the concentration of the acceptor ions and  $x$  is a normalized time variable given by  $x = DC^{-1/3} t^{2/3}$ . Here,  $D$  and  $C$  are the diffusion coefficient and the interaction parameter, respectively.

Figure 7 shows the decay curve of the sample doped with 0.5 mol% Tm<sup>3+</sup> ions ( $N_A = 1.39 \times 10^{20}$ ). The solid curve is obtained by doing a non-linear least-squares fit to the experimental data with equation (3). For this sample, the best-fit values of  $C$  and  $D$  were determined to be  $0.515 \times 10^{-38} \text{ cm}^6 \text{ s}^{-1}$  and  $2.44 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ , respectively. A useful parameter which provides insight about the strength of cross relaxation is the critical distance  $R_0$ .  $R_0$  is defined as the distance at which the probability of the cross-relaxation process becomes equal to the intrinsic decay rate of the metastable level and can be calculated in terms of  $C$  and  $\tau_R$  from

$$R_0^6 = \tau_R C. \quad (4)$$

The critical distance indicates that the energy transfer can occur among ions located within this distance. Hence greater critical distance values mean faster energy transfer via cross relaxation. Table 2 lists the best-fit values of  $C$ ,  $D$  and  $R_0$  for various samples used in our study. Note that  $R_0$  values range from 12.7 to 25.2  $\text{\AA}$  with an average of 17.9  $\text{\AA}$ . For comparison, the average  $R_0$  for the 0.7TeO<sub>2</sub>:0.3CdCl<sub>2</sub> glass host determined in this study is much larger than the 7.3  $\text{\AA}$  value which was recently reported in the case of the thulium-doped Ge<sub>30</sub>Ga<sub>2</sub>As<sub>6</sub>S<sub>62</sub> glass [9].

#### 4. Conclusions

In conclusion, we have presented the results of a spectroscopic study that investigates the effect of cross relaxation on the strengths of the 1470 and 1800 nm emissions in Tm<sup>3+</sup>-doped



**Table 2.** Best-fit values of the cross-relaxation parameters  $D$ ,  $C$  and  $R_0$  (see equation (3) in the text) at different  $\text{Tm}^{3+}$  ion concentrations.

$\text{Tm}^{3+}$ concentration (mol%)	$\text{Tm}^{3+}$ ion concentration $N_A$ ( $\text{cm}^{-3}$ )	$D$ ( $\text{cm}^2 \text{s}^{-1}$ )	$C$ ( $\text{cm}^6 \text{s}^{-1}$ )	$R_0$ ( $\text{Å}$ )
0.05	$1.43 \times 10^{19}$	$9.61 \times 10^{-11}$	$31 \times 10^{-38}$	25.2
0.1	$2.93 \times 10^{19}$	$5.54 \times 10^{-11}$	$1.65 \times 10^{-38}$	15.5
0.25	$7.10 \times 10^{19}$	$3.69 \times 10^{-11}$	$4.12 \times 10^{-38}$	18.0
0.5	$1.39 \times 10^{20}$	$2.44 \times 10^{-11}$	$0.515 \times 10^{-38}$	12.7

( $0.70\text{TeO}_2:0.3\text{CdCl}_2$ ) glass. Samples with five different thulium concentrations were prepared and measurements were performed to determine the relative strength of the emission bands, decay lifetimes and the luminescence quantum efficiencies. Results show that at a thulium concentration of around 0.1 mol%, the integrated strengths of these emission bands are nearly equal. As the thulium concentration is increased, the strength of the 1470 nm emission decreases in relation to the 1800 nm emission because of cross relaxation. The luminescence quantum efficiencies were also found to decrease with increasing ion concentration. Cross relaxation occurs as a result of the strong coupling between the  $\text{Tm}^{3+}$  ions and favours 1800 nm emission at higher ion concentrations. This may be particularly important in the construction of Tm-based fibre lasers operating at 1800 nm since it provides an effective mechanism to depopulate the  $^3\text{F}_4$  upper level and transfer the energy to the 1800 nm emission. The mechanism for the energy transfer was found to be diffusion-limited cross relaxation. Finally, the average critical distance parameter  $R_0$  was determined to be 17.9 Å, much larger than that for the  $\text{Ge}_{30}\text{Ga}_2\text{As}_6\text{S}_{62}$  glass host.

### Acknowledgment

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