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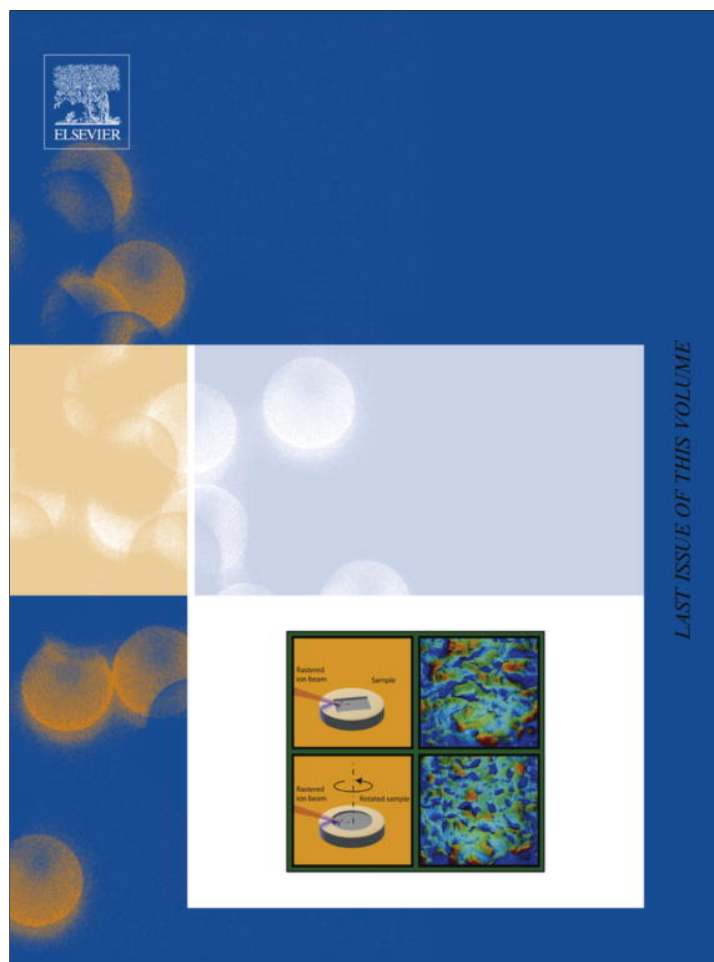


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ABSTRACT

Electronic absorption, excitation and time-resolved emission spectra of Tb^{3+} in the cubic elpasolite host lattice Cs_2NaYF_6 show that the 5D_3 – 5D_4 cross-relaxation is due to an electric quadrupole–electric dipole mechanism. The donor Tb^{3+} ion transits from 5D_3 to 5D_4 whilst the acceptor ion transits from 7F_6 to 7F_2 with the emission of an odd-parity phonon.

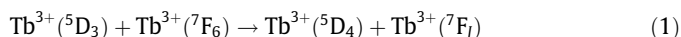
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1. Introduction

In lasers and phosphor materials, lanthanide ions (Ln^{3+}) are doped into transparent host lattices with low phonon energy in order to minimize nonradiative processes. For concentrated materials, energy migration between Ln^{3+} may finally populate traps or killer sites, and this is known as *concentration quenching* of emission [1]. Alternatively, the reduced separation between Ln^{3+} in concentrated materials may serve to promote energy transfer up- or down-conversion between ions when the donor–acceptor energies match and the relevant transition selection rules permit transfer to occur. The down-conversion can serve a useful purpose, such as changing ultraviolet into visible photons. Many documented energy transfer mechanisms involve resonant electric dipole (ED) transitions at the donor and acceptor sites (ED–ED mechanism), with a spectral overlap of donor emission and acceptor absorption [2]. However this mechanism is not possible when Ln^{3+} are situated at centrosymmetric sites, such as in the elpasolite lattice Cs_2NaLnF_6 [3] unless odd-parity vibrations are involved in the nonresonant energy transfer. The general theory of phonon-assisted energy transfer has been developed by Kushida [4] and Holstein et al. [5], and the application to centrosymmetric systems [6] indicated that the participation of odd-parity phonons could play an important role.

We therefore targeted the concentration quenching of terbium (Tb^{3+}) emission from the 5D_3 state in the centrosymmetric elpasolite host as a case-study for the investigation of the quenching mechanism. This system is attractive for study because the detailed $4f^8$ crystal field energy level scheme is available from two-photon excitation studies [3]. Some previous studies have

investigated the concentration quenching of 5D_3 emission in non-centrosymmetric systems. For $CaSc_2O_4:Tb^{3+}$ [7], $CaYAlO_4:Tb^{3+}$ [8] and $LaAlGe_2O_7:Tb^{3+}$ [9], the 5D_3 quenching was attributed to the cross-relaxation:



where $J = 0$, with critical concentration of 1 at.% for the latter system. The cross-relaxation Eq. (1) was otherwise thought to involve $J = 1$ for $LiYF_4:Tb^{3+}$ [10] and $J = 2$ for $(Lu,Y)SiO_5:Tb^{3+}$ [11]. The energy transfer mechanism was deduced to be electric dipole–electric dipole (ED–ED) for $Y_3Al_5O_{12}:Tb^{3+}$ [12], α -GdOF [13] and for $LiYF_4:Tb^{3+}$ above 70 K [10], but electric quadrupole–electric quadrupole (EQ–EQ) at 4.2 K for $LiYF_4:Tb^{3+}$. From a detailed consideration of the crystal field energy levels for the systems $CsCdBr_3$, $CsMgBr_3$ and $CsMgCl_3$ doped with Tb^{3+} at a C_{3v} site [14], it was concluded that the cross-relaxation mechanism involved resonant ‘hot’ transitions and that phonon-assisted processes were not important. As mentioned above, since dipole–dipole processes are forbidden for $Cs_2NaYF_6:Tb^{3+}$ unless they are phonon-assisted, it was of interest to investigate the 5D_3 concentration quenching in this system in view of the above conclusions.

2. Experimental

Crystals of $Cs_2NaY_{1-x}Tb_xF_6$ ($x = 0.1$ and 0.01) were purchased from Dr. N.M. Khaidukov, who synthesized them by a hydrothermal method. Electronic absorption and emission spectra were recorded at Fuzhou using an Edinburgh Instruments spectrometer.

Time-resolved emission spectra at room temperature were recorded at CityU using the spectral mode on an Edinburgh Instruments LP920-KS instrument equipped with an ICCD detector. The excitation source for the time-resolved emission measurement was the third harmonic output (355 nm; 6–8 ns fwhm pulse width) of a Spectra-Physics Quanta-Ray Q-switched LAB-150 pulsed Nd-YAG laser (10 Hz).

* Corresponding author. Fax: +852 3442 0506.

E-mail addresses: duanck73@hotmail.com (C.-K. Duan), bhtan@cityu.edu.hk (P.A. Tanner).¹ Present address: College of Physics and Mathematics, Chongqing University of Post and Telecommunications, Chongqing 400 065, China.

3. Results and discussion

The electronic ground state of Tb^{3+} is the $^7\text{F}_6$ multiplet. This ion occupies only one type of site of O_h point group symmetry in Cs_2NaYF_6 and the distortion from cubic symmetry is not spectroscopically evident in $\text{Cs}_2\text{NaY}_{0.9}\text{Tb}_{0.1}\text{F}_6$ at the investigated temperatures. The room temperature absorption spectrum, Figure 1(a), contrasts the absorption intensity exhibited by intraconfigurational $4f^8-4f^8$ and interconfigurational $4f^8-4f^75d$ transitions of Tb^{3+} in $\text{Cs}_2\text{NaY}_{0.9}\text{Tb}_{0.1}\text{F}_6$. The latter transitions are identified as spin-forbidden ($4f^75d$ HS: high spin) and spin-allowed ($4f^75d$ LS: low spin) in the figure, whilst the intraconfigurational $^7\text{F}_6-^5\text{D}_4$ transition is only visible in the expanded scale spectrum, Figure 1(c). The 10 K excitation spectrum monitoring emission from $^5\text{D}_4$, Figure 1(b) exhibits a marked sharpening of features. The $^5\text{D}_4$ term, marked in Figure 1(c), splits into $A_{1g} + T_{1g} + E_g + T_{2g}$ (O_h) crystal field levels, and has the lowest level (A_{1g}) located at $20\,672\text{ cm}^{-1}$. Since the energy gap below $^5\text{D}_4$ is $14\,442\text{ cm}^{-1}$ [3], i.e. spanned by 31 phonons, it is intensely luminescent. By contrast, the smallest gap below the next highest multiplet, $^5\text{D}_3$, is ($^5\text{D}_3 A_{2g}-^5\text{D}_4 T_{2g}$) 5545 cm^{-1} (spanned by 12 phonons) [3]. From the rule of thumb that a suitably-populated multiplet term will luminesce if the gap below it is spanned by more than four phonons, luminescence is also expected from $^5\text{D}_3$. However, since the $\text{Tb}^{3+} 7\text{F}_j$ ($J=6-0$) multiplets extending up to 6230 cm^{-1} , the possibility exists that $^5\text{D}_3$ can be quenched by cross-relaxation energy transfer to a Tb^{3+} neighbour.

Under 355 nm excitation of Tb^{3+} in $\text{Cs}_2\text{NaTbF}_6$, the vibronic sideband of $^5\text{G}_5$ is populated. Rapid ($<1\text{ ns}$) nonradiative decay then occurs to the luminescent $^5\text{D}_3$ multiplet. Using this excitation wavelength, the luminescence spectra of $\text{Cs}_2\text{NaYF}_6:\text{Tb}^{3+}$ (10 at.% and 1 at.%) between 410 nm and 640 nm are shown in Figure 2. Some of the terminal multiplets are marked in the figure. It can be seen that at 10 K, the intensity ratio for emissions from $^5\text{D}_3$ to those from $^5\text{D}_4$ of the 1 at.% Tb^{3+} sample is much larger than that for the 10 at.% sample. This shows a much faster decay of $^5\text{D}_3$ in the 10 at.% sample due to cross relaxation. It is also evident that the lowest energy transitions from $^5\text{D}_3$ form a spectral overlap with the absorption bands of $^5\text{D}_4$.

We have analyzed the decay kinetics of emission from $^5\text{D}_3$ and $^5\text{D}_4$ at room temperature for the $\text{Cs}_2\text{NaY}_{0.9}\text{Tb}_{0.1}\text{F}_6$ sample. Figure 3 shows some emission snapshots at various times following the 355 nm laser pulse. Again, the population of $^5\text{D}_4$ from $^5\text{D}_3$ is evident and the $^5\text{D}_3$ emission has disappeared at 15 ms. The decay curves were measured for $^5\text{D}_3$ emission (at 381 nm and 439 nm) and $^5\text{D}_4$ emission (at 553 nm and 489 nm) and the results are shown in Figure 4. The decay from $^5\text{D}_4$ is monoexponential with a long lifetime typical of Ln^{3+} in elpasolite hosts: $13.6 \pm 0.2\text{ ms}$.

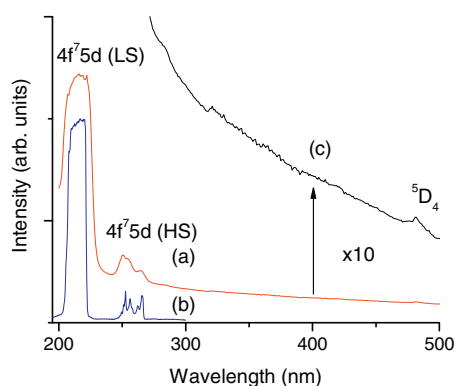


Figure 1. Room temperature absorption spectrum (curve (a)) and enlarged curve (c) and 10 K excitation spectrum by monitoring 540 nm emission from $\text{Cs}_2\text{NaYF}_6:\text{Tb}^{3+}$ of 10 at.% Tb^{3+} . The absorption curve shows not only f-d transitions, but also the $^7\text{F}_6-^5\text{D}_4$ f-f transition.

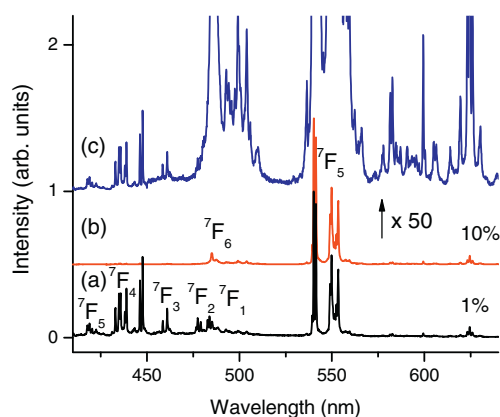


Figure 2. 10 K emission spectra of $\text{Cs}_2\text{NaY}_{1-x}\text{Tb}_x\text{F}_6:\text{Tb}^{3+}$ with $x = 0.01$ (curve (a)) and $x = 0.1$ (curve (b)), with an enlargement in curve (c).

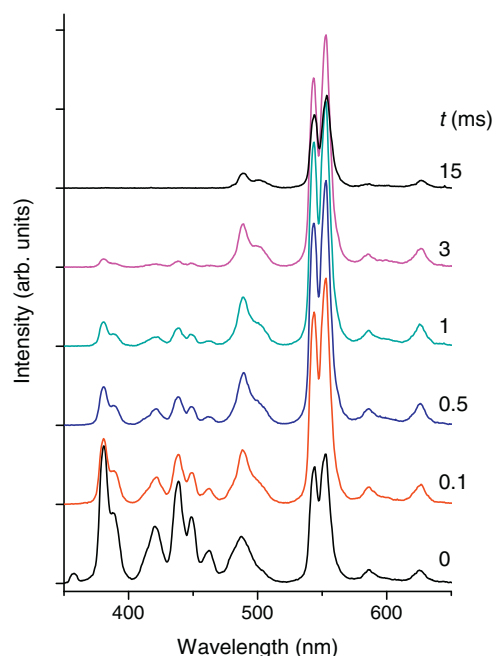


Figure 3. Snapshots of the room temperature emission spectra of $\text{Cs}_2\text{NaY}_{0.9}\text{Tb}_{0.1}\text{F}_6$ at time t after 355 nm pulsed excitation.

The decay of $^5\text{D}_3$ is clearly non-monoexponential. It can be fitted ($R^2 = 0.995$) by biexponential decay with the lifetimes of 0.059 ms and 1.176 ms, but no physical meaning can be attached to this. Instead, we prefer to employ a cross-relaxation model where back-transfer is not possible due to the large donor–acceptor energy difference. Then, the luminescence decay of $^5\text{D}_3$ is due to two contributions: (i) the cross-relaxation process, which is characterized by a temporal parameter, τ_{CR} ; (ii) the one-site radiative and nonradiative decay, which is characterized by the parameter, $\tau_{\text{one-site}}$. The decay curves can then be written in the form of a modified Inokuti–Hirayama equation [15] as:

$$I(t) = I_0 \exp(-(t/\tau_{\text{CR}})^{3/s} - t/\tau_{\text{one-site}}) \quad (2)$$

where I_0 is the intensity at $t = 0$ and s is a parameter to describe distance dependence of the cross-relaxation. It is observed from the fitting that the decay of $^5\text{D}_3$ is well-simulated by $s = 7.5$, $\tau_{\text{CR}} = 0.3\text{ ms}$, and $\tau_{\text{one-site}} = 7.5\text{ ms}$. In order not to obtain excessive data-points, the early parts of the decay in Figures. 4(a,b) were

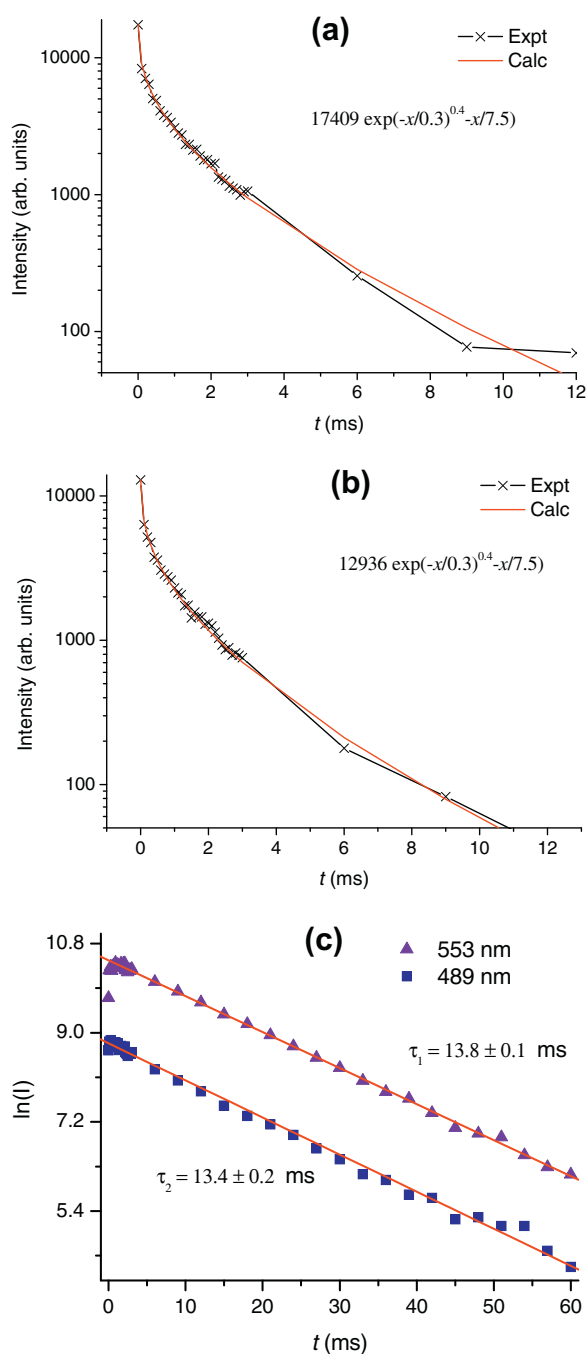


Figure 4. Decay curves for (a) 381 nm emission, (b) 439 nm emission, and (c) 553 nm and 489 nm emissions of Tb^{3+} under 355 nm pulsed excitation. The expressions for the calculated curves and the fitted lifetimes are given in the plot.

well-sampled, but the sampling interval was set to be longer for the later part of the decay. Thus, the $\tau_{\text{one-site}}$ value, which is determined by the tail of Figure 4(a,b), is not accurate, but the fitted value is consistent for both emission wavelengths. The values 6, 8, or 10 of the parameter s can be taken to indicate the mechanism ED–ED, EQ–ED, or EQ–EQ of the process. In the present case, the EQ–ED mechanism is indicated.

The detailed crystal field level analysis of the cross-relaxation pathway from $^5\text{D}_3$ for $\text{Cs}_2\text{NaYF}_6:\text{Tb}^{3+}$ indicates that since the maximum and minimum energy differences between $^5\text{D}_3$ and $^5\text{D}_4$ are 5822 cm^{-1} and 5545 cm^{-1} , the value of J in Eq. (1) must be 2. Furthermore, since the cross-relaxation is efficient at 10 K, it is most likely that the $^5\text{D}_3$ donor level is the lowest level, A_{2g}

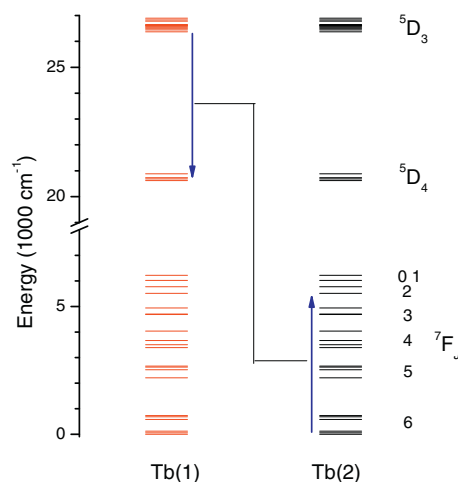


Figure 5. Cross-relaxation mechanism for the quenching of $^5\text{D}_3$ emission in $\text{Cs}_2\text{NaTbF}_6$. Note the scale break in energy.

$26\,383\text{ cm}^{-1}$. Then, considering the $^5\text{D}_4$ and $^7\text{F}_2$ crystal field level schemes [3], the transfer must be nonresonant. Following the EQ–ED mechanism, it is only feasible that the EQ transition $\Delta S = 0$; $|\Delta L| \leq 2$; $|\Delta J| \leq 2$ takes place between $^5\text{D}_3$ and $^5\text{D}_4$ since $^7\text{F}_6$ – $^7\text{F}_2$ is EQ forbidden. Furthermore, point group selection rules restrict the possible transitions to $^5\text{D}_3 A_{2g} (26\,383)$ – $^5\text{D}_4 E_g (20\,740)$ or $^5\text{D}_4 T_{1g} (20\,711)$, where the energies are cm^{-1} . These deductions are firm, whereas some tentative conclusions can be made concerning the $^7\text{F}_6$ – $^7\text{F}_2$ part of the process. This ED transfer step must involve an odd-parity phonon, which is most likely a moiety optical mode. From the analysis of the $^7\text{F}_2$ energy levels, the most likely vibration is the $\nu_6 \tau_{2u}$ mode, which is observed at $\sim 122, 133\text{ cm}^{-1}$ in the vibronic sideband, with a FWHM $\sim 30\text{ cm}^{-1}$. A candidate for the electric dipole vibronic transition is then deduced to be $^7\text{F}_6 A_{1g} (0) \rightarrow ^7\text{F}_2 T_{2g} (5522) + \nu_6 (122, 133)$, where the energies (in cm^{-1}) are in parentheses. The cross-relaxation mechanism is depicted in Figure 5.

4. Conclusions

Optical spectroscopic properties of Tb^{3+} ion at the O_h site in the cubic host Cs_2NaYF_6 have been studied at both room temperature and 10 K. The room temperature absorption spectrum shows spin-allowed and spin-forbidden 4f–5d transitions, and at the lower energy side, weak 4f–4f transitions. The 4f–5d absorption peaks are prominent in the 10 K excitation spectrum monitoring the 540 nm $^5\text{D}_4$ emission of Tb^{3+} for $\text{Cs}_2\text{NaY}_{0.9}\text{Tb}_{0.1}\text{F}_6$ samples. Time-resolved spectroscopy at room temperature clearly shows the decreasing intensity variation of $^5\text{D}_3$, compared with the $^5\text{D}_4$ emission, with increasing time delay. The $^5\text{D}_3$ emission, when monitored at 381 nm or 439 nm, exhibits non-exponential decay curves, whereas the decay of $^5\text{D}_4$ is monoexponential and the decay lifetime is longer. Numerical simulations indicate that the non-exponential decay of $^5\text{D}_3$ is due to a cross relaxation of the EQ–ED type, where the donor Tb^{3+} ion relaxes from $^5\text{D}_4$ to $^5\text{D}_3$ in an EQ allowed transition, and at the same time the acceptor Tb^{3+} ion is promoted from $^7\text{F}_6$ to $^7\text{F}_2$ together with the emission of an odd-parity phonon. It is noticed that the $^7\text{F}_6$ to $^7\text{F}_2$ transition of the acceptor is not EQ allowed unless J -mixing is considered.

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