Energy transfer processes in $\text{K}_5\text{Li}_2\text{GdF}_{10}:\text{Eu}, \text{Pr}$

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Abstract

In $\text{K}_5\text{Li}_2\text{Gd}_{0.80}\text{Pr}_{0.10}\text{Eu}_{0.10}\text{F}_{10}$ the $^5\text{D}_{1,0}$ luminescence of europium is quenched by the presence of Pr^{3+} . Analysis of the decay curves of the $^5\text{D}_0$ and $^5\text{D}_1$ luminescence, recorded at room temperature, suggests that the $\text{Eu}^{3+} \rightarrow ^5\text{D}_0$ emission is quenched by quadrupole–quadrupole interaction with $^1\text{D}_2$ multiplet of praseodymium. The generalized Yokota–Tanimoto model has been used to explain the behavior of the decay curves and to determine the kinetic microparameters C_{DA} , related to the cross relaxation, and D , related to the energy migration probabilities. The “critical radius” (R_0) for these interaction was calculated to be in the range 10.007–11.528 Å.

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1. Introduction

The quantum-cutting discovered by Meijerink is limited by the difficulty of coupling light into weak, parity forbidden Gd^{3+} transitions within the $4f^7$ configuration, especially the $^6\text{G}_J$ or situated above (Wegh et al., 1999; Liu et al., 2003). Thus, an additional sensitizer is needed which can absorb the VUV radiation and transfer it to active ions to improve efficiency of a phosphor. Recently, heavy metal like Pb^{2+} was proposed as a Gd^{3+} sensitizer (Babin et al., 2004). Tm^{3+} as a sensitizer was found to be not efficient in $\text{LiGdF}_4:\text{Tm}, \text{Eu}$ (Peijzel et al., 2004). In $\text{K}_5\text{Li}_2\text{Gd}_{0.80}\text{Pr}_{0.10}\text{Eu}_{0.10}\text{F}_{10}$ an efficient energy transfer from the excited broad 5d band of Pr^{3+} to Gd^{3+} ions was discovered. What is more, further co-operative energy transfer, originated in the $^6\text{P}_J$ state of gadolinium to the $^5\text{D}_0$ multiplets of two Eu^{3+} , which by passes the $^5\text{D}_1$ level, was observed (Solarz and Ryba-Romanowski, 2006). Thus, theoretically it should be possible, joining the Dexter’s (1957) and Wegh’s (1999) processes, to obtain three visible photons from Eu^{3+} per a photon used for excitation. In such a system the $^6\text{G}_J$ multiplets of Gd^{3+} should be excited in matrix without Pr^{3+} ions or the Pr^{3+} f–d band must be situated above the $^6\text{G}_J$ state. In such a case, one

photon could be obtain in cross-relaxation of $\text{Gd} \rightarrow ^6\text{G}_J$ with $\text{Eu} \rightarrow ^7\text{F}_1$ – $^5\text{D}_0$ (or ordinary emission from $^6\text{G}_J$ to $^6\text{P}_J$). Next, due to the co-operative energy transfer process, two photons could be emitted from two Eu ions excited to the $^5\text{D}_0$ multiplet via $1 \times ^6\text{P}_J$ – $^8\text{S}_{7/2} \approx 2 \times ^7\text{F}_1$ – $^5\text{D}_0$.

Most of bibliographic data describes the microparameters of non-radiative energy transfer processes due to dipole–dipole (D – D) approximations. In some of them the possibility of higher order processes, like dipole–quadrupole (D – Q) or quadrupole–quadrupole are considered (de Sousa et al., 2002). This paper deals with the energy transfer processes, in the visible part of electromagnetic spectrum in $\text{K}_5\text{Li}_2\text{Gd}_{0.80}\text{Pr}_{0.10}\text{Eu}_{0.10}\text{F}_{10}$ crystal, from the europium $^5\text{D}_0$, $^5\text{D}_1$ to the praseodymium $^1\text{D}_2$ multiplet. Such transfers, to our knowledge, were not investigated in the past.

2. Experimental

Single $\text{K}_5\text{Li}_2\text{Gd}_{0.80}\text{Pr}_{0.10}\text{Eu}_{0.10}\text{F}_{10}$ crystal was grown by vertical Bridgman method in graphite crucibles made from high quality IG-110 purified graphite. The crystal is orthorhombic (space group D_{2h}^{16} —Pnma). Its structure is built from layers perpendicular to the a -axis, formed by LnF_8 dodecahedra and LiF_4 tetrahedra. Lanthanide and lithium ions occupy sites with point C_s symmetry, whereas potassium and fluorine ions occupy sites with C_s and C_1 symmetry. The LnF_8 polyhedra do not share

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fluorine ions and the closest lanthanide ions are separated by more than 6.5 Å. Owing to these features, exchange interactions between Ln ions may be neglected. Based on crystallographic structure, there is only one site for the lanthanide ions.

The room temperature, excitation spectra were done with a DongWoo Optron Co. setup, which assembles DM711 and DM152i monochromators equipped with a Xe Arc lamp DL180-Xe. As the detector a Hamamatsu R-955 PMT was used. The low temperature excitation spectrum was measured in HasyLab at DESY in Hamburg in Germany, using SUPER-LIMI station setup. The analyzed signal was cut off at above 19000 cm⁻¹ with an edge filter. In luminescence decay time measurements, short (4 ns) pulses delivered by the optical parametric oscillator OPO (Continuum, Surelite I) pumped by the third harmonic of Nd:YAG laser were used to excite directly luminescence levels. The luminescence was dispersed by 1 m double-grating monochromator GDM-1000, detected by the Hamamatsu R-928 PMT. The decay signal was averaged and stored with the Tektronix TDS 3052 digital oscilloscope; all decay data were composed of ten thousand points. The fits of experimental decay curves were done using the Microcal Origin v5.0 software; the amplitude of the curves was calibrated to a thousand.

3. Results and discussion

Fig. 1 presents the room temperature excitations spectra of K₅Li₂Gd_{0.80}Pr_{0.10}Eu_{0.10}F₁₀ recorded at 588, 604 and 613 nm (transitions: Eu³⁺⁵D₁ → ⁷F₃, Pr³⁺³P₀ → ³H₆, and Eu³⁺⁵D₀ → ⁷F₂, respectively). In this matrix, the luminescence from the praseodymium ¹D₂ level, for concentration higher than 3 at%, is quenched entirely, and was not observed also in the K₅Li₂Gd_{0.80}Pr_{0.10}Eu_{0.10}F₁₀. Upon direct excitation of Eu³⁺-f multiplets or Pr³⁺ lower then the f–d transitions, only a typical emission from Pr³⁺ or Eu³⁺ levels can be observed. It means that in the range above 20 000 cm⁻¹, and below 31 000 cm⁻¹ there is no energy transfer between different (Eu, Gd, Pr) activators in this matrix, or the efficiency of it is small. In the region 32 000–35 000 cm⁻¹, one can see, the spectra recorded at 588 and 613 nm are different. The difference shows that excitation of Gd³⁺ states promotes emission from the ⁵D₀ europium level and the energy transfer process bypasses the ⁵D₁ state (Solarz and Ryba-Romanowski, 2006). The lowest spectrum in Fig. 1 (recorded at 8 K) for the ⁵D₀ → ⁷F₂ emission in K₅Li₂LaF₁₀:Eu 25 at%, confirms that the difference between spectra recorded at 588 and 613 nm can be assigned to Gd excitation.

The lifetime of Eu³⁺, ⁵D₀ (12 000 μs) in europium doped K₅Li₂LaF₁₀ and K₅Li₂GdF₁₀ was found to be independent of concentration up to 50 at%, within the experimental errors (Solarz and Ryba-Romanowski, 2003), and decrease slightly for higher concentration. What is more, the decay curves are pure exponential. Addition of Pr³⁺ in an amount of 10 at% to the crystal containing 10 at% of Eu³⁺, changes the character of decay curves to non-exponential. Therefore, it is impossible to calculate the real lifetime, basing on decay curve, and only

Fig. 1. Excitation spectra of luminescence of K₅Li₂Gd_{0.80}Pr_{0.10}Eu_{0.10}F₁₀ recorded 588, 604, 613 nm (17007, 16556 and 16313 cm⁻¹). The lowest part of the figure represents UV excitation spectrum of the ⁵D₀ → ⁷F₂ emission (613 nm) in K₅Li₂La_{0.75}Eu_{0.25}F₁₀ crystal.

mean lifetime (τ_m) given as

$$\tau_m = \frac{\int_{t=0}^{\infty} I dt}{I_0} \quad (1)$$

can be obtained. The I_0 is the intensity at the beginning of decay curve and t represents time. For the Eu³⁺ ⁵D₀ multiplet, in K₅Li₂Gd_{0.8}Pr_{0.1}Eu_{0.1}F₁₀, such calculated mean lifetime is 1390 μs. Similar dependence was found for ⁵D₁ multiplet. Its lifetime shortens from 3000 to 2070 μs. The values 12 000 and 3000 μs was used in further calculations as radiative lifetimes.

Non-exponential decay curves give the possibility to determine the nature of ion–ion interaction (dipole–dipole D–D, dipole–quadrupole D–Q or quadrupole–quadrupole Q–Q). To characterise it, the generalized model of Inokuti and Hirayama (1965) was used.

In this model the experimental decay curve can be described as

$$I(t) = \text{Offset} + I(0) \exp \left(-\frac{t}{\tau_r} - C_A Q t^{3/S} \right), \quad (2)$$

where Q is the energy transfer parameter, Offset describes the y-axis shift of experimental curve and S defines the multipolar mechanism and it is: 6 for D–D, 8 for D–Q, 10 for Q–Q kind of electrostatic interaction. The C_A parameter represents the concentration of active ions, in this case—Eu³⁺ ions. Q is given

Table 1

The kinetic microparameters, C_{DA} and D related to the cross-relaxation and to the energy migration in $K_5Li_2Gd_{0.80}Pr_{0.10}Eu_{0.10}F_{10}$

Model	Concentration (at%) (ions/m ³)	Multiplet	S	R_0 (m ⁻¹⁰)	C_{DA} (mS/s)	$\pm\Delta C_{DA}$ (mS/s)	D (m ² /s)	$\pm\Delta D$ (m ² /s)	χ^2
Inokuti and Hirayama	10 3.463×10^{26}	⁵ D ₀	6	10.007	8.2936×10^{-53}	3.6843×10^{-55}	–	–	279.641
			8	10.774	1.4987×10^{-70}	4.7833×10^{-73}	–	–	95.006
			10	11.255	2.6942×10^{-90}	8.6729×10^{-91}	–	–	68.233
		⁵ D ₁	6	10.408	4.2369×10^{-52}	1.0070×10^{-54}	–	–	144.135
			8	11.095	7.6564×10^{-70}	2.3564×10^{-72}	–	–	156.941
			10	11.528	1.3820×10^{-87}	7.5056×10^{-90}	–	–	341.114
			6	10.007	8.2937×10^{-53}	3.6846×10^{-55}	9.8266×10^{-31}	1.8759×10^{-22}	279.672
		⁵ D ₀	8	–	–	–	–	–	–
			10	11.255	2.6942×10^{-88}	1.3203×10^{-90}	1.1285×10^{-25}	8.4197×10^{-20}	68.240
			6	10.408	4.2369×10^{-52}	5.4623×10^{-55}	1.5234×10^{-31}	–	134.150
Yokota and Tanimoto	10 3.463×10^{26}	⁵ D ₁	8	10.787	6.1097×10^{-70}	4.2705×10^{-72}	2.1490×10^{-17}	6.2370×10^{-19}	135.112
			10	10.723	6.6999×10^{-88}	7.075×10^{-90}	8.5598×10^{-17}	1.1605×10^{-18}	178.019

The R_0 represents “critical radius”. Fig. 2. The best fit of theoretical curves to experimentally recorded decay curves of luminescence from the ⁵D₀ and ⁵D₁ multiplets. For details, see Table 1.

by formula

$$Q = \frac{4\pi}{3} \Gamma \left(1 - \frac{3}{S} \right) (C_{DA}^{(S)})^{3/S}. \quad (3)$$

Formula 2 describes the quenching mechanism only if the migration is absent.

If the migration occurs one can use the generalization of Yokota and Tanimoto (1967) expression, given by Martin et al. (1999):

$$I(t) = \text{Offset} + I(0) \exp \left[-\frac{t}{\tau_r} - C_A Q t^{3/S} \left(\frac{1 + a_1 X + a_2 X^2}{1 + b_1 X} \right)^{S-3/S-2} \right], \quad (4)$$

where a_1 , a_2 and b_1 are the Padé approximation coefficients, dependent on the multipolar character of the interaction

(see Martin et al., 1999 for their values) and

$$X = D C_{DA}^{-2/S} t^{1-2/S}, \quad (5)$$

where D is the diffusion coefficient that characterizes the energy transfer processes between ions. If D is zero (the migration between ions are negligible) the Inokuti and Hirayama formula is obtained.

The energy transfer probability, between donors and acceptors, can be expressed by

$$W_{i-i}(R_K) = \frac{C_{DA}^{(S)}}{R_K^S}, \quad (6)$$

where the R_K is the mean separation between donor and acceptor. The R_K for which the W_{i-i} is equal to A_r is commonly called “critical radius” (R_0).

The values of fitting parameters are presented in the Table 1. The decay curves of luminescence from the 5D_0 and 5D_1 multiplets and theoretical best fit to them is presented in Fig. 2. One can see that the nature of the 5D_0 luminescence quenching can be determined as the quadrupole–quadrupole interaction.

The best fit was obtained in the simple Inokuti and Hirayama model (no migration) although in the frame of the generalized Yakota and Tanimoto model, the calculated chi-squared (χ^2) is rather the same. The worst fit for the 5D_0 was for dipole–dipole interaction. It was not possible to start fitting procedure in the generalized Yakota and Tanimoto model, for dipole–quadrupole interactions, because for all given values of D parameter, their values did not change during iterations. Therefore, they are omitted in the Table 1. In the case of determining the nature of the 5D_1 quenching the best fit was obtained for the D–D interaction between activators. The contribution of D–Q interaction could not be rejected, however.

Based on Pr, Eu energies of crystal-field levels in $K_5Li_2PrF_{10}$ and $K_5Li_2EuF_{10}$ (Sokólska et al., 2000; Solarz and Ryba-Romanowski, 2003) the $Eu^{3+} ^5D_{0,1}$ emission can be quenched with $Pr^{3+} ^1D_2$ level via the cross-relaxation patterns: (i) $^5D_0 \rightarrow ^7F_{0,1,2} \cong ^3H_4 \rightarrow ^1D_2$ and (ii) $^5D_1 \rightarrow ^7F_{2,3,4} \cong ^3H_4 \rightarrow ^1D_2$. Such transitions are resonant with emission of phonons. In the matrix cut off phonon energy was determined to be 680 cm^{-1} .

In all analyzed interaction obtained values or “critical radii” (R_0) are in the range of $10.007\text{--}11.528\text{ \AA}$. It means that there is need to reduce statistical concentration of Pr^{3+} , in this crystal to 3.9 at% at least, to make non-radiative process less probable than radiative one. At this 10 at% solution of Pr^{3+} , praseodymium ions act as killer for europium $^5D_{0,1}$ emission which can lessen the positive influence of this ion in UV–VUV part of spectrum. At such a lower concentration of Pr^{3+} the emission from the $Pr^{3+} ^1D_2$ may appear in the red part of visible emission.

4. Conclusions

The interactions between excited the $Eu^{3+} ^5D_0$ and 5D_1 levels with the $Pr^{3+} ^1D_2$ level were analyzed. It seems that for the $^5D_0\text{--}^1D_2$ the interaction is quadrupole–quadrupole, whereas for the $^5D_1\text{--}^1D_2$ it is dipole–dipole. The “critical radius” (R_0) for these interaction was calculated to be $10.007\text{--}11.528\text{ \AA}$. It gives the possibility to use a Pr^{3+} as a sensitizer for the

Gd^{3+}/Eu^{3+} quantum cutting couple but the concentration of Pr^{3+} should be at least 2.5 times lower than that in the analyzed $K_5Li_2Gd_{0.80}Pr_{0.10}Eu_{0.10}F_{10}$.

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