Energy Transfer between Tb$^{3+}$ and Eu$^{3+}$ in LaPO$_4$: Pulsed versus Switched-off Continuous Wave Excitation

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The energy transfer (ET) between Tb$^{3+}$ and Eu$^{3+}$ is investigated experimentally and with available theoretical models in the regime of high Tb$^{3+}$ concentrations in ≈30 nm LaPO$_4$ nanoparticles at room temperature. The ET efficiency approaches 100% even for lightly Eu$^{3+}$-doped materials. The major conclusion from the use of pulsed laser excitation and switched-off continuous wave laser diode excitation is that the energy migration between Tb$^{3+}$ ions, situated on La$^{3+}$ sites with ≈4 Å separation, is not fast. The quenching of Tb$^{3+}$ emission in singly doped LaPO$_4$ only reduces the luminescence lifetime by ≈50% in heavily doped samples. Various theoretical models are applied to simulate the luminescence decays of Tb$^{3+}$ and Tb$^{3+}$, Eu$^{3+}$-doped LaPO$_4$ samples of various concentrations and the transfer mechanism is identified as forced electric dipole at each ion.

1. Introduction

Lanthanide ions present unique spectral properties, including long lifetime, multiple narrow and well-separated bands, and large effective shifts from excitation to emission wavelength. They can be model candidates as donor and acceptor in the study of energy transfer (ET). Hence, there have been a plethora of ET research studies concerning lanthanide ions, such as between the tripositive ions Ce-Eu,[1] Ce-Tb,[2] Tb-Eu,[3] Pr-Yb,[4] Ce-Gd,[5,6] Sm-Eu,[6-8] and Ho-Yb,[9,10] with the focus upon the applied optical properties of phosphors, such as the color tunability of luminescence and optical thermometry. However, Dutra et al.[11] have pointed out that in 2015 less than 3% of published studies concerning lanthanide ions made use of theoretical tools. In particular, the ET between Tb$^{3+}$ and Eu$^{3+}$ has attracted much attention (Table S4, Supporting Information). The $5D_4$ donor state emission from Tb$^{3+}$ is quenched and instead red emission from the Eu$^{3+}$ $7D_0$ state is observed when exciting into a Tb$^{3+}$ absorption band. The detailed energy transfer mechanism is not clear in many cases. For example, Moran et al.[12] studied the cubic system Cs$_3$NaYCl$_6$ doped with Tb$^{3+}$ and Eu$^{3+}$ in a wide range of concentrations at 298 and 77 K. It was concluded that discrepancies between the calculated and experimental rate parameters are large, notably by four or five orders of magnitude for multipole–multipole mechanisms. Whereas it could be possible that different interaction mechanisms take part in different solid-state lattices, various studies have attributed the interaction mechanism between Tb$^{3+}$ and Eu$^{3+}$ to electric dipole–electric dipole (ED–ED)[13–16] or electric dipole–electric quadrupole (ED–EQ)[17] or exchange interaction.[18,19] The $5D_4 \rightarrow 7F_J$ ($J = 6–4$) transitions of Tb$^{3+}$ are forced ED allowed whereas the $5D_0 \rightarrow 7F_0$ transition of Eu$^{3+}$ is dipole forbidden,[20] but at room temperature the $5D_0 \rightarrow 7F_1$ forced ED pathway is also available. The term forced (or induced) ED refers to 4f–4f transitions being enabled via the wavefunction mixture with 5d (or higher) opposite-parity configurations through the crystal field symmetry or vibrations of the appropriate symmetry. Furthermore, the energy migration between the donor Tb$^{3+}$ ions has been stated as very fast[21] or slow,[22] for example, Blasse[23] envisaged that the migration rate between lanthanide ions such as Eu$^{3+}$ or Gd$^{3+}$ was up to $10^7$ s$^{-1}$ for a separation of 4 Å, whereas Dornauf and Heber[24] found negligible concentration quenching of Tb$^{3+}$ in La$_2$SiO$_4$. The process of migration between identical ions leads to an increase in lifetime, whereas termination of the process at a trap leads to a decrease.

The kinetics of an ET process as a function of concentration have been studied by several authors, for example, by Fong and Diestler[25] and Lupei.[26] A linear relation between the energy transfer rate and acceptor concentration has been taken to indicate a two-ion process, whereas a quadratic
performed this for LaPO₄ doped with Tb³⁺ prior to an ET study involving two lanthanide ions, and we have utilized micrometer-sized samples synthesized at high temperature (Table S4, Supporting Information). We prepared nanomaterials doped with Tb³⁺ and Eu³⁺ because the occurrence of trap species, if important, would then be magnified in our study. We take the previous study of Chen and co-workers on similar size nanoparticles of Eu³⁺-doped hexagonal hydrated TbPO₄ as a reference for comparison of our results obtained from nanomaterials prepared by a modified method of Haase and co-workers. The relevant energy level schemes of Tb³⁺ and Eu³⁺ are displayed in Figure 2a.

The major aims of our study were to investigate (i) the importance of energy migration between terbium ions in the LaPO₄ host, where the donor–donor separation is about 4 Å; and (ii) to give a quantitative description of Tb³⁺-Eu³⁺ ET in this host lattice, where complications such as charge inequality and multisite occupation of the ions are absent. With the use of different excitation techniques and various theoretical models, these aims have been fully addressed.

2. Theoretical Section

Various models have been employed to simulate the donor decay after pulsed excitation when energy is transferred from a donor to acceptor ions in order to ascertain the interaction mechanism. We largely focus upon ED–ED energy transfer because the relevant lanthanide ion transitions are of forced electric dipole character. The donor emission intensity at time t, relative to the initial intensity, when in the presence of an acceptor, is given by

\[
I_D(t) = I_D(0) \exp \left[ -\left( \frac{t}{\tau_D} + k_{ET} \right) \right]
\]

where \(\tau_D\) is the lifetime of donor in the absence of the acceptor and \(k_{ET}\) is the energy transfer rate (=\(P_{DA} A\)), where \(P_{DA}\) is a parameter describing the donor–acceptor interaction and \(A\) is the acceptor concentration). This equation holds for an isolated donor–acceptor pair, or for an acceptor in an average donor environment due to rapid energy migration between donors. In the absence of donor–donor migration, the decay is not monoeponential because the acceptors at sites \(q\) are situated at different distances.

![Figure 1. Tb³⁺-Eu³⁺ energy transfer rates for some systems with low Eu³⁺ concentrations from literature data, fitted by \(y = A + Bx^2\) (blue lines) and \(y = C + Dx\) (red lines): (a) Cs₂NaTb₁₋ₓEuₓCl₆ at 293 K, \(x = 0.065 \pm 0.004, B = 42.7 \pm 0.04, A = 0.9930\); (b) TlY₂₋ₓEuₓF₁₀ at 295 K, \(x = 0.0596 \pm 0.0017, B = 9.0 \pm 0.3, A = 0.9956\); (c) Cs₂NaY₀.₉₉₅₋ₓTbₓ₀.₀₀₅EuₓCl₆ at 295 K, \(x = 14.28 \pm 1.7, B = 0.10 \pm 0.05, A = 0.948; \) (d) Cs₂NaTb₁₋ₓEuₓCl₆ at 80 K, \(x = 15.6 \pm 1.6, B = 0.03 \pm 0.01, A = 0.928\). The linear fittings are shown in red and in green for the reduced range of \(x\)Eu in (c). Note the superior quadratic fittings in (a), (b) and the linear fits in (c), (d).](image-url)
It is clear that the sum over $X_0$ represents the total donor–acceptor transfer rate. In the continuum approximation (which predicts excessive energy transfer rates at very small donor–acceptor separations), the Inokuti–Hirayama model \cite{34} for multipole interactions assumes a random arrangement of acceptors and the intensity of emission at time $t$ is related to that initially by

$$I_0(t) = I_0(0) \exp\left\{-\frac{1}{\tau_D} \prod_l \left[1 - c_l \exp\left(-X_{sl}\right)\right]\right\}$$

where $s = 6, 8, 10$ according to the electric multipolar mechanism ED–ED, ED–EQ, or EQ–EQ, respectively; $\Gamma$ is the gamma function; $c_l = (x \times Z)/V$, where $x$ is the stoichiometric mole fraction, $Z$ is the number of acceptors in the unit cell, and $V$ is its volume; $c_0$ is the critical (reduced) acceptor concentration

$$c_0 = \frac{3}{4\pi R_0^2}$$

where $R_0$ is the critical distance. Instead, if transfer is considered to shells of acceptor ions in a crystal \cite{24}

$$I_0(t) = I_0(0) \exp\left\{-\frac{t}{\tau_D} \exp\left\{-\frac{4\pi R_0 c_l t}{\tau_D}\right\}\right\}$$

where $l'$ is the total number of acceptor sites present in shell $l$ at distance $l' R$ from the donor; $Z$ is the total number of sites in $k$ shells; and $x$ is the acceptor molar concentration. $N$ is the total number of acceptors $= Z x$. The second exponential function represents a correction factor for acceptors outside the chosen shells. The other symbols are defined above.

An alternative description of the shell model for small ($\approx 3 \text{ nm}$) spherical nanoparticles, based upon the master Equation (2), and correcting for the proximity of the donor to the surface, has been given by Rabouw et al.\cite{35,36} This equation is not necessary in the present case since our particles are rather larger.
In Equations (2), (3), and (5), no account is taken of donor–donor migration or donor–acceptor back transfer. The presence of 3D energy migration may be examined by the analysis of the (monoeponential) donor decay lifetime, \( \tau \), at very long times after the excitation pulse, the asymptotic behavior \((t \to \infty)\)

\[
I_D(t) = I_D(0) \exp\left[\frac{-(t-\tau)}{\tau}\right], \quad \text{where} \quad \frac{1}{\tau} = \frac{1}{\tau_D} + \frac{1}{\tau_{DF}} \tag{6}
\]

where, in this case, \( \tau_D \) represents the intrinsic donor lifetime and for weak diffusion (when the donor–donor migration rate is smaller than the donor–acceptor transfer rate), with the rate \( k_{DF} = 1/\tau_{DF} \)

\[
\frac{1}{\tau_{DF}} = 4\pi \epsilon_A D \rho \quad \text{and} \quad \rho = 0.68(C/D)^{1/4} \tag{7}
\]

Here, \( D \) is a diffusion constant and \( C \) is a donor–acceptor interaction constant. Alternatively, for weak diffusion, the simplest equation for the inclusion of migration between donor ions, for the case of ED–ED interaction is\[37\]

\[
I_D(t) = I_D(0) \exp\left\{-\frac{1}{3} \pi^2 \epsilon_A \left(\frac{\alpha_{DA}^0}{\tau_D}\right)^2 \left\{1 + \frac{\alpha_{DA}^0 \tau_D + \beta_x^2}{1 + \beta_x^2}\right\}\right\} \tag{8}
\]

where \( \alpha_1 = 10.866, \alpha_2 = 15.500, \beta = 8.743; \quad x = D(\alpha_{DA}^0)^{-1/3} \tau_D^{1/3}. \quad D \) is a diffusion constant and \( \alpha_{DA}^0 \) is the ED–ED interaction parameter for donor–acceptor transfer \( (= \alpha_{DA}^0/\tau_D) \). Analogous equations have been given for donor–acceptor exchange interaction, and for the occurrence of migration for types of interaction other than ED–ED, and the reader is referred to the original publications for details\[24,34,37,38\]. In principle, the fitting of donor decay by these equations yields the interaction mechanism, the critical distance \((\text{i.e., when the rate of ET is equal to the donor decay rate})\), and the magnitude of the diffusion constant. When the donor–donor migration rate exceeds that of donor–acceptor transfer, a random hopping model is more appropriate\[39\].

The above equations refer to the donor emission profile after a short excitation pulse. The donor emission decay profile following switched-off continuous excitation has been discussed by Eisenthal and Siegel\[40\] and Siebold and Heber\[41\]. Pulsed excitation provides an instantaneous population of randomly excited donors at \( t = 0 \) (cf. Equation (3)) with the acceptor ions unexcited. By contrast, switched-off continuous excitation gives the steady-state population of excited donors. In this case, the excited donors are not randomly distributed—the probability of an excited donor being near an acceptor is smaller than that of an excited donor with an acceptor further away. The donor decay will therefore differ from the case of pulsed excitation unless very rapid migration of energy occurs between the donors. Assuming a random population of unexcited donors and acceptors, in the absence of donor–donor migration, the donor decay at time \( t \), after switched-off continuous excitation at time \( t = 0 \), can be represented in the case of ED–ED transfer by\[40\]

\[
I(t) = I(0) \left\{\exp\left(-\frac{t}{\tau}\right) - 2q \left(\frac{t}{\tau}\right)^{1/2} \exp\left(q^2\right) \left[1 - \text{erf} \left[q + \left(\frac{t}{\tau}\right)^{1/2}\right]\right]\right\} \tag{9a}
\]

where

\[
q = (N_A/2)(R_0/R_f)^{3/2} = \left(\frac{3}{2}\right)\left(\frac{\epsilon_A}{\epsilon_n}\right) \tag{9b}
\]

and

\[
\text{erf}(x) = \frac{2}{\pi^{1/2}} \int_0^x \exp(-y^2)dy \tag{9c}
\]

Here, \( \tau \) is the donor lifetime in the absence of acceptors; \( N_A \) is the number of unexcited acceptors; \( R_0 \) is the critical transfer distance for which the probability of nonresonance deactivation and resonance transfer is equal for a donor–acceptor pair; and \( R_f \) is the vessel radius. The donor decay under the same conditions for pulsed excitation is given by Equation (3).

3. Results and Discussion

3.1. Structure and Morphology of the Crystals

The morphology of La\(0.10\)Tb\(0.90\)PO\(4\) (i) and La\(0.02\)Tb\(0.90\)Eu\(0.08\)PO\(4\) (ii) nanocrystals, together with the high-resolution transmission electron microscopy (HRTEM) image of the latter (iii) are presented in Figure 2b. The nanocrystals are elongated compared with the size of the LaPO\(4\) nanocrystals prepared by Haase and co-workers\[31\], which is due to the decreasing amount of the complexing agent triethyl phosphate employed\[30\]. The HRTEM image displays lattice fringes with spacing 0.5 nm for most particles which indicates a highly crystalline material. The measured average size of the nanocrystals is 30 nm compared with that of 34 nm determined from the line broadening in the X-ray diffraction (XRD) pattern (Figure 2c). The XRD pattern is consistent with the standard monoclinic card of TbPO\(4\) with a shift of the peaks to lower angles since Eu\(^{3+}\) is a slightly larger ion than Tb\(^{3+}\). No additional peaks of other phases are present. The structure of the monoclinic form TbPO\(4\) (space group \(P2_1/c\), \(Z = 4\)) is shown in Figure 2d and is the same structure for the other lanthanide ions from La to Gd. The closest distance between the nine-coordinate Tb\(^{3+}\) ions, with site symmetry \(C_s\), is 3.97 Å. There is another form of TbPO\(4\) belonging to the tetragonal space group \(I4_1/amd\)\[43\] with Tb\(^{3+}\) ions situated at sites of \(D_4d\) point group symmetry, with closest separation 3.79 Å.

The Fourier transform infrared (FTIR) spectra in Figure 2e show the characteristic phosphate group vibrations at (in cm\(^{-1}\)): 543 (\(v_9\)), 956 (\(v_4\)), and 1086 (\(v_3\))\[44\]. The band at 3326 cm\(^{-1}\) is characteristic of the O–H stretching vibration of H\(_2\)O. The bands at 1457 cm\(^{-1}\) are due to the coating of TOA.
3.2. The Decay of Tb$^{3+}$ Emission in LaPO$_4$:Tb$^{3+}$

The luminescence decay of the Tb$^{3+}$ 5D$_4$ state was monitored for LaPO$_4$ doped with various concentrations of Tb$^{3+}$, by exciting at 485 nm and collecting the emission of the 5D$_4$ $\rightarrow$ 7F$_5$ transition at 543 nm. The decay curves for switched-off continuous wave (cw) and for pulsed excitation are shown on a log scale in Figure 3a for one sample of La$_{0.10}$Tb$_{0.90}$PO$_4$ and show a distinct difference in the initial decay. The time width of the excitation pulse, in the microsecond regime, is therefore smaller than the energy migration hopping time. If the migration rate were fast, then the curves would be superimposable. The decay following cw excitation can be fitted by a monoexponential function in the region from 0 to 15 ms with the lifetime 1.556 ± 0.001 ms ($R^2 = 0.99933$) whereas that for pulsed excitation can be fitted by biexponential decay with the above fixed lifetime and another one of 0.258 ± 0.001 ms ($R^2 = 0.99908$). The decay after cw excitation represents the steady state of the migration and energy transfer to traps, whereas pulsed excitation provides an equal excitation probability for all donors. Hence, the difference could be due to the fact that some donors are near traps, that is, energy acceptors of a different species. The nature of the traps is subsequently discussed. The decays were fitted by Equation (9a) (for switched-off cw excitation, Figure 3b, $R^2 = 0.9992$) and Equation (3) (for pulsed excitation, Figure 3c, $R^2 = 0.9984$) using two variable parameters in each case. From these fits, the derived ratios of $c_A/c_0$ are 0.64 (cw) and 0.63 (pulsed), which give an acceptor concentration between $2.3 \times 10^{21}$ and $4.5 \times 10^{19}$ cm$^{-3}$ for $R_0$ values between 4 and 15 Å, respectively.

The decay curves following pulsed excitation for Tb$^{3+}$ in La$_{1-x}$Tb$_x$PO$_4$, after logarithmic transformation, are reasonably linear in the measured region from 0 to 20 ms, with $R^2 > 0.998$, except for La$_{0.10}$Tb$_{0.90}$PO$_4$ with $R^2 > 0.9963$, as shown in Figure 4a. The 5D$_4$ lifetime data for all samples are summarized in Table S1 (Supporting Information) and demonstrate a monoexponential decrease in lifetime with increasing concentration of Tb$^{3+}$ in La$_{1-x}$Tb$_x$PO$_4$ (Figure 4b). The lifetime of the La$_{0.10}$Tb$_{0.90}$PO$_4$ nanocrystals (≈1.5 ms) is considerably longer than that reported at room temperature as 0.55 ms for TbPO$_4$ nanowires (2 µm $\times$ 40 nm) [45] and 0.98 ms for micrometer-size TbPO$_4$[29] so that surface quenching in these latter two examples is clearly very important. The lifetime of a La$_{0.98}$Tb$_{0.02}$PO$_4$ bulk sample[46] was reported to be 3.1 ms which is similar to the measured lifetime of 3.04 ms for La$_{0.999}$Tb$_{0.001}$PO$_4$ nanocrystals herein.

The use of Equation (1), where $\tau_D$ in this case is the lifetime at infinite dilution and $k_{ET}$ is the ET rate to traps, gives a linear relation of $k_{ET}$ with concentration (Figure 4c), which can be interpreted as showing that a two-body process is responsible for quenching: Tb$^{3+}$ – trap. The ET rate is slow: being only $\approx 350$ s$^{-1}$ for the La$_{0.10}$Tb$_{0.90}$PO$_4$ sample. Recently, Johnson et al. have argued that migration to killer sites (i.e., nonradiative sinks) is more important than cross-relaxation processes.[47] This alternative quenching process: cross-relaxation involving
two or three \cite{48} Tb\textsuperscript{3+} ions is not possible when considering the Tb\textsuperscript{3+} energy level scheme in Figure 2a since the energy gap below 5D\textsubscript{4} is nearly 15 000 cm\textsuperscript{-1}. Fitting the long-term decay curves with Equation (6) enables the determination of 1/τ\textsubscript{DP}, which is also not fast. This parameter gives a linear plot against Tb\textsuperscript{3+} concentration, as expected from Equation (7) (Figure S1, Supporting Information).

More detailed fits to the decay curves of La\textsubscript{1-x}Tb\textsubscript{x}PO\textsubscript{4} were then carried out. Figure 5a,\textsubscript{b} shows the section of Tb\textsuperscript{3+} emission decay in the range from 0 to 4 ms with monoeXponential (green), biexponential (red), and Inokuti–Hirayama, Equation (3) (blue), fittings for x = 0.9, 0.7. The Inokuti–Hirayama equation refers to energy transfer from a donor to a random array of acceptor ions without donor–donor migration. This model gives a poorer fit to the data. The biexponential fit is superior to the linear fit described above and was repeated for other Tb\textsuperscript{3+} concentrations with the results listed in Table S2 (Supporting Information). The biexponential fit is explained by the occurrence of two different environments of Tb\textsuperscript{3+} ions. In their study, van Hest et al.\cite{46} have associated two environments of Eu\textsuperscript{3+} in 3.9 nm nanocrystals of LaPO\textsubscript{4} with surface (τ = 1.9 ms) and interior (τ = 4.7 ms) sites since the amplitudes if their fit were 44 and 56%, respectively. The occurrence of several sites for Eu\textsuperscript{3+} in La\textsubscript{0.98}Eu\textsubscript{0.02}PO\textsubscript{4} was previously reported from 77 K emission spectra by Dexpert-Ghys et al.\cite{49} who pointed out that in Tb\textsuperscript{3+} ions at the microsecond level and this is rationalized in terms of slow energy migration and the different decay of Tb\textsuperscript{3+} at two different crystal environments. The quenching of emission with increasing Tb\textsuperscript{3+} concentration is only moderate and emission is strong even in the 90% Tb\textsuperscript{3+}-doped sample.

Considering the crystal structure of TbPO\textsubscript{4} (Figure S2, Supporting Information), the migration between Tb\textsuperscript{3+} ions is expected to be 3D. Consideration of the selection rules for \textsuperscript{7}F\textsubscript{6}–5D\textsubscript{4} migration\cite{20} shows that it is forbidden to first order by the exchange mechanism and although spin-forbidden to first order, it could be due to the EQ–EQ or ED–ED mechanisms, where ED represents forced electric dipole.

### 3.3. Energy Transfer from Tb\textsuperscript{3+} to Eu\textsuperscript{3+} in the LaPO\textsubscript{4} Host

#### 3.3.1. Electronic Spectra

We have investigated the scenario of high Tb\textsuperscript{3+} donor concentrations in the ET from Tb\textsuperscript{3+} to Eu\textsuperscript{3+}. Figure 6a shows the excitation spectrum of La\textsubscript{0.93}Eu\textsubscript{0.07}PO\textsubscript{4} when monitoring the Eu\textsuperscript{3+} 5D\textsubscript{0} → 7F\textsubscript{4} emission at 697 nm. All features but one correspond to transitions from the electronic ground state to 4f\textsuperscript{6} excited states of Eu\textsuperscript{3+}, with the strongest band at 393 nm corresponding to 7F\textsubscript{6} → 7L\textsubscript{6}. The broad feature with maximum at 265 nm is the Eu-O charge transfer band. Notice that there is no Eu\textsuperscript{3+} absorption band near 480–500 nm so when exciting this sample with 485 nm radiation, as Figure 6b shows on an expanded ordinate scale, there are no emission bands present. The excitation spectrum of La\textsubscript{0.10}Tb\textsubscript{0.90}PO\textsubscript{4}, Figure 6c exhibits the 7F\textsubscript{6} → 5D\textsubscript{4} absorption band at 485 nm, together with transitions to higher excited 4f\textsuperscript{8} states of Tb\textsuperscript{3+}, and to 4f\textsuperscript{5}5d\textsuperscript{1} at 260 nm. Note the absence of the broad, strong band at 316 nm observed by Chen and co-workers.\cite{29} Hence, when exciting La\textsubscript{0.10}Tb\textsubscript{0.90}PO\textsubscript{4} at 485 nm, Figure 6d, the emission corresponds to 5D\textsubscript{4} → 7F\textsubscript{j} transitions, with the strongest being with J = 5 at 543 nm. The excitation spectrum, Figure 6e, of

![Figure 4. a) Luminescence decay curves; b) monoeXponential lifetimes (τ\textsubscript{ex}); c) energy transfer rates (k\textsubscript{ET}) of La\textsubscript{1-x}Tb\textsubscript{x}PO\textsubscript{4} nanocrystals (λ\textsubscript{ex} = 485 nm, λ\textsubscript{em} = 543 nm).](image-url)
the codoped sample La$_{0.02}$Tb$_{0.90}$Eu$_{0.08}$PO$_4$ when monitoring the Eu$^{3+}$ emission from $^5$D$_0$ exhibits features of both Eu$^{3+}$ and Tb$^{3+}$, thereby demonstrating ET from Tb$^{3+}$ to Eu$^{3+}$. Now, when exciting into the Tb$^{3+}$ absorption band at 485 nm in La$_{0.02}$Tb$_{0.90}$Eu$_{0.08}$PO$_4$ (Figure 6f), the emission from Tb$^{3+}$ is mainly quenched and all bands correspond to Eu$^{3+}$ $^5$D$_0 \rightarrow ^7$F$_J$ transitions. The time-resolved spectra of La$_{0.05}$Tb$_{0.90}$Eu$_{0.05}$PO$_4$ show that the quenching of Eu$^{3+}$ emission (due to efficient energy transfer from Tb$^{3+}$ to Eu$^{3+}$) is more complete compared with La$_{0.75}$Tb$_{0.20}$Eu$_{0.05}$PO$_4$ (Figure S3, Supporting Information).
There is no obvious emission from Tb$^{3+}$ in La$_{0.05}$Tb$_{0.90}$Eu$_{0.05}$PO$_4$ even when the delay time is only 100 ns.

### 3.3.2. Efficiency of Energy Transfer

The efficiency of ET from Tb$^{3+}$ to Eu$^{3+}$ in La$_{0.10}$-xTb$_{0.90}$Eu$_{x}$PO$_4$ was calculated by two methods. Figure 7a shows the decay curves of Tb$^{3+}$ emission in La$_{0.10}$-xTb$_{0.90}$Eu$_{x}$PO$_4$ nanocrystals and the fitted monoexponential lifetime decreases from 1.6 ms ($x = 0$) with increasing of Eu$^{3+}$ mole ratio to 0.01 ms ($x = 0.1$) (Table 1, column 2). If the decay is monoexponential, the energy transfer rate from Tb$^{3+}$ to Eu$^{3+}$ is given by the difference between the decay rate of donor when in the presence and absence of acceptor $[1/\tau_D] - [1/\tau_{D0}]$. These values are listed in column 4 of Table 1 and span from 8 to 99 ms$^{-1}$. When the decay curve is not monoexponential, the average decay time, $\tau_D'$, can be expressed as $\tau_D' = \int t \frac{I(t)}{I(0)} dt$. The energy transfer rate is then calculated according to column 5 of Table 1. The similarity of values in columns 4 and 5 shows that the deviation from Tb$^{3+}$ monoexponential decay in La$_{0.10}$-xTb$_{0.90}$Eu$_{x}$PO$_4$ nanocrystals is relatively small. The relationship between the concentration of Eu$^{3+}$ and the ET rate calculated by the two methods is plotted in Figure 7c. The linear relation demonstrates that the ET involves one Tb$^{3+}$ ion and one Eu$^{3+}$ ion and is not a three-body process. The efficiency of ET from Tb$^{3+}$ to Eu$^{3+}$ achieves 99% for $x = 0.05$ (Table 1, column 6) and the ET rate is quite fast, 4.9 × 10$^4$ s$^{-1}$, accounting for the near-monoexponential decay in Figure 7a.

![Figure 7](image_url)

**Figure 7.** Luminescence decay curves of La$_{0.10}$-xTb$_{0.90}$Eu$_{x}$PO$_4$ nanocrystals: a) Tb$^{3+}$ emission: $\lambda_{ex} = 485$ nm, $\lambda_{em} = 543$ nm) and b) Eu$^{3+}$ emission: $\lambda_{ex} = 485$ nm, $\lambda_{em} = 697$ nm. Notice the logarithmic ordinate scale in (a). The inset in (b) shows the decay at shorter times for the samples of La$_{0.05}$Tb$_{0.90}$Eu$_{0.01}$PO$_4$ and La$_{0.05}$Tb$_{0.90}$Eu$_{0.05}$PO$_4$. c) Energy transfer rate from Tb$^{3+}$ to Eu$^{3+}$ in La$_{0.10}$-xTb$_{0.90}$Eu$_{x}$PO$_4$ as a function of mole fraction of Eu$^{3+}$ calculated by two methods.

| $x$     | $\tau_D$ [ms] | $k_D$ [ms$^{-1}$] | $k_E$ [ms$^{-1}$] | $\eta$ [%] |
|---------|---------------|-------------------|-------------------|---------|
| 0.01    | 1.6           | 0.625             | 0                 | 0       |
| 0.02    | 1.01          | 9.09              | 8.47              | 8.90    |
| 0.05    | 0.058         | 17.24             | 16.62             | 16.16   |
| 0.08    | 0.020         | 50                | 49.38             | 48.32   |
| 0.1     | 0.015         | 66.67             | 66.04             | 63.16   |
| 0.1     | 0.010         | 100               | 99.38             | 91.86   |

Table 1. Summary of Tb$^{3+}$ lifetime ($\tau_D$), decay rate ($k_D$), energy transfer rate ($k_E$), and efficiency ($\eta$) of La$_{0.10}$-xTb$_{0.90}$Eu$_{x}$PO$_4$ nanocrystals ($\lambda_{ex} = 485$ nm, $\lambda_{em} = 543$ nm). For $x = 0$, $k_D = k_{D0}$. 

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samples. The curves have been fitted by biexponential decay functions representing a donor–acceptor process in Figure S4 (Supporting Information). The donor lifetime was set as that in column 2 of Table 1. At low Eu$^{3+}$ concentrations, the build-up process from population by Tb$^{3+}$5D4 is clearly visible (refer to the inset in Figure 7b for x = 0.01). However, with increasing x the Tb$^{3+}$ decay is faster and the build-up is too fast to be observed in the figures (Figure S4, Supporting Information, x = 0.05-0.10). The fitted 5D0 Eu$^{3+}$ lifetime does not change greatly—from 1.61 ms for x = 0.01 to 1.28 ms for x = 0.10—but the variation can be fitted by a monoexponential function (Figure S4f, Supporting Information). The depopulation of the Eu$^{3+}$5D0 state is also due to a two-body process (Figure S4g, Supporting Information).

### 3.4. Migration and Mechanism of Energy Transfer between Tb$^{3+}$ and Eu$^{3+}$

As discussed above for La$_{0.10}$Tb$_{0.90}$PO$_4$, the rate of excitation migration between Tb$^{3+}$ ions is not fast. The 5D4 Tb$^{3+}$ emission decays after pulsed and switched-off continuous wave excitation in the Tb$^{3+}$Eu$^{3+}$ doped system are displayed on a logarithmic ordinate scale in Figure 8a and show that the migration rate between Tb$^{3+}$ ions is slower than the microsecond time scale. The fits to the curves using Equations (9a) and (3) are shown on a linear scale in Figure 8b and from the determined ratio of $c_A/c_0$, both give the critical distance $R_0$ as 17 Å using Equation (4). Attempts to calculate the diffusion constant using the Yakota–Taminoto Equation (8), requiring one fixed and four variable parameters, were unsuccessful because there are too many parameters and the fits are not unique.

Two models were employed to investigate the ET mechanism for the entire series of La$_{0.10-x}$Tb$_{0.90}$Eu$_x$PO$_4$ luminescence decays of Tb$^{3+}$. The Inokuti–Hirayama equation (Equation (3)) gave the superior fits for s = 6 (Figure 8c, Table 2). This ET model is based on the assumption that there is a continuous distribution of the acceptor sites around the donors. Dornhauf and Heber$^{[24]}$ derived the model, Equation (5), in which the “permitted” donor–acceptor separations are determined.

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**Figure 8.** a) The decay curves of La$_{0.09}$Tb$_{0.90}$Eu$_{0.01}$PO$_4$ after pulsed and cw excitation. b) Fits to these curves on a linear ordinate scale using Equation (9a) for cw and Equation (3) for pulsed excitation. Fits for the series La$_{1-x}$Tb$_{0.90}$Eu$_x$PO$_4$ using c) the Inokuti–Hirayama equation, Equation (3) and d) the Dornhauf–Heber equation, Equation (5). e) Sensitivity of the fits using Equation (5) to the number of shells employed, for La$_{0.02}$Tb$_{0.98}$Eu$_{0.00}$PO$_4$. 

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3.5. Color Variation on Doping LaPO₄ with Tb³⁺ and Eu³⁺

Figure 9 shows the CIE chromaticity coordinates \((x, y)\) for three samples of the doped LaPO₄ nanocrystals. The singly Tb³⁺-doped materials exhibit green emission \((x = 0.37, y = 0.62)\) but the color changes to orange for the doubly doped nanocrystals: \((x = 0.48, y = 0.51)\) for \(\text{La}_{0.05}\text{Tb}_{0.90}\text{Eu}_{0.05}\text{PO}_4\) and \((x = 0.52, y = 0.48)\) for \(\text{La}_{0.02}\text{Tb}_{0.90}\text{Eu}_{0.08}\text{PO}_4\).

4. Conclusions

Luminescence quenching by migration of the excitation energy throughout the lattice which terminates at trap sites often limits the concentration of doped lanthanide ions in a solid-state material to less than a few mol%. The energy migration in highly doped materials has been stated as very fast or slow by the structure of the crystal lattice. Table S3 (Supporting Information) gives the radial distances from a donor ion to the acceptor sites in the first 80 shells in the LaPO₄ host lattice and the number of acceptor sites in each shell. For this system, the number of discrete lattice sites around the donor was taken to be \(Z = 115\). This corresponds to a sphere with radius \(R = 12.4863\) Å. The curves can be well-fitted with Equation (5) only when \(s = 6\) which means that the multipolar mechanism is ED–ED transfer. (Figure 8d) The latter fits used two adjustable parameters, \(I_0(0)\) and \(R_0\), and the values of \(R_0\) are listed in Table 3. The critical transfer distances values vary over a narrow range and are slightly smaller than the values calculated in Table 2 using the Inokuti–Hirayama equation, Equation (3), with \(\tau_0 = 0.00148\) s.

Table 2. Fits of Tb³⁺ emission decay in \(\text{La}_{0.10}\text{Tb}_{0.90}\text{Eu}_{0.08}\text{PO}_4\) using the Inokuti–Hirayama equation, Equation (3), with \(\tau_0 = 0.00148\) s.

| \(\text{La}_{0.10}\text{Tb}_{0.90}\text{Eu}_{0.08}\text{PO}_4\) | \(c_4 [A^{-1}]\) | \(s\) | \(R_0 [Å]\) | \(R^2_{adj}\) |
|--------------------------|----------------|--------|------------|------------|
| 0.01                     | 0.00015        | 3.44   | 4.22 \times 10^{-5} | 17.82       | 0.9898      |
| 0.02                     | 0.00029        | 5.61   | 5.18 \times 10^{-5} | 16.64       | 0.9927      |
| 0.05                     | 0.00073        | 11.78  | 6.16 \times 10^{-5} | 15.71       | 0.9801      |
| 0.08                     | 0.00115        | 15.08  | 7.70 \times 10^{-5} | 14.58       | 0.9863      |
| 0.10                     | 0.00145        | 20.04  | 7.24 \times 10^{-5} | 14.88       | 0.9363      |

Table 3. Fits of emission decay of Tb³⁺ in \(\text{La}_{0.10}\text{Tb}_{0.90}\text{PO}_4\) using the Dornauf–Heber equation (Equation (5)): \(\tau_0 = 0.00148\) s, \(Z = 115\) discrete lattice sites arranged in 80 shells.

| \(\text{La}_{0.10}\text{Tb}_{0.90}\text{PO}_4\) | \(c_4 [A^{-1}]\) | \(s\) | \(R_0 [Å]\) | \(R^2_{adj}\) |
|--------------------------|----------------|--------|------------|------------|
| 0.01                     | 0.00015        | 6      | 14.61      | 0.9931      |
| 0.02                     | 0.00029        | 6      | 14.61      | 0.9931      |
| 0.05                     | 0.00073        | 6      | 14.61      | 0.9931      |
| 0.08                     | 0.00115        | 6      | 14.61      | 0.9931      |
| 0.10                     | 0.00145        | 6      | 14.61      | 0.9931      |
the migration rate of 339 s$^{-1}$ found in Sr$_3$Tb$_{0.90}$Eu$_{0.10}$(PO$_4$)$_3$.[50] where the Tb–Tb distance is also 4 Å.

The mechanism of ET between Tb$^{3+}$ and Eu$^{3+}$ has been previously studied with conflicting results, which claimed that ED–ED,[13–16] ED–EQ,[17] or exchange[18,19] is the dominant interaction mechanism. Naturally, the mechanism may depend upon the crystal structure, determining the site symmetries of these ions and the distance between them. In the present study, the energy transfer mechanism between Tb$^{3+}$ and Eu$^{3+}$ has been studied systematically by different models and found to be ED–ED, where ED represents the forced electric dipole mechanism.

The efficiency of ET from Tb$^{3+}$ to Eu$^{3+}$ approaches 100% even for lightly doped Eu$^{3+}$ samples (Table 1). The ET rate is $=10^3$ s$^{-1}$ for Tb$_{0.90}$Eu$_{0.10}$PO$_4$, and (from Table 3) the donor–acceptor ET parameter $\alpha_{31}$ is calculated to be $4.3 \times 10^{-19}$ cm$^6$ s$^{-1}$. This value is considerably greater than those for Y$_2$O$_3$:Tb$^{3+}$, Eu$^{3+}$ (2.0 $\times$ 10$^{-21}$ cm$^6$ s$^{-1}$)[32] and Sr$_3$Tb$_{0.90}$Eu$_{0.10}$(PO$_4$)$_3$ (4.8 $\times$ 10$^{-21}$ cm$^6$ s$^{-1}$).[50] The luminescence decay of Tb$^{3+}$ can be well-fitted by a model, which neglects diffusion and follows the ED–ED mechanism. The very efficient ET between Tb$^{3+}$ and Eu$^{3+}$ was previously reported for hexagonal hydrated TbPO$_4$:Eu$^{3+}$ nanocrystals.[29] We also concur with this study that diffusion does not play a major role in this ET process, but we do not observe fast energy migration in singly Tb$^{3+}$-doped LaPO$_4$. In future, we will examine the ET between Tb$^{3+}$ and Eu$^{3+}$ in the regime of low Tb$^{3+}$ concentrations.

5. Experimental Section

**Synthesis of LaPO$_4$:Tb$^{3+}$, Eu$^{3+}$ Nanomaterials:** The materials employed and their purity are listed in the Supporting Information. La$_{1-x}$Tb$_x$PO$_4$ ($x = 0.001, 0.05, 0.10, 0.20, 0.30, 0.50, 0.70, 0.90$) and La$_{0.10}$Tb$_{0.90}$Eu$_{0.10}$PO$_4$ ($y = 0.01, 0.02, 0.05, 0.08, 0.10$) nanoparticles were prepared by a modified method of Haase and co-workers.[30,31] A clear solution of 1 mmol lanthanide chlorides (LaCl$_3$, TbCl$_3$, EuCl$_3$) in 1 mL of distilled water was added to a 10 mmol aqueous solution of NaOH, Na$_2$CO$_3$, or Na$_2$SiO$_3$. The mixture was warmed to 65 °C for 3 h under nitrogen and then cooled to room temperature. The precipitate was filtered and washed with methanol two times, and dried under vacuum.

**Instrumental Methods:** X-ray diffraction patterns of crystals were recorded with a Bruker AXS D8 Advance X-Ray Diffractometer equipped with a non-monochromated Cu Kα X-ray source ($\lambda = 1.5418$ Å). TEM and HRTEM images were obtained by a Tecnai G2 20 S-TWIN Transmission Electron Microscope. Infrared spectra were recorded at room temperature in the range 400–4000 cm$^{-1}$ using a Perkin Elmer Paragon 1000 PC spectrometer with resolution of 4 cm$^{-1}$. The electronic emission and excitation spectra were recorded by a Hamamatsu Fluorolog-3 spectrophotometer using a 450 W continuous xenon lamp as the light source and the signal was detected by a Hamamatsu R928 photomultiplier. Luminescence lifetimes were measured by a digital phosphor oscilloscope (DSO9104A Oscilloscope) from Agilent Technologies: 1 GHz, 20 GSa s$^{-1}$) with a Nd:YAG pulsed laser as excitation source, a third-order harmonic generator (120 mJ), and an optical parameter oscillator (OPO, Spectra-Physics versaScan and UVScan: pulse duration 8 ns, repetition frequency 10 Hz). Continuous wave excitation was provided by a 488 nm laser power (MDL-III-488L-20 mW) with a shut-off time of 25 μs (Figure S5, Supporting Information).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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[1] L. Zhou, W. Zhou, F. Pan, R. Shi, L. Huang, H. Liang, P. A. Tanner, X. Du, Y. Huang, Y. Tao, L. Zheng, Chem. Mater. 2016, 28, 2834.
[2] K. Kornepe, H. Borchert, J. Storz, A. Lobo, S. Adam, T. Moller, M. Haase, Angew. Chem., Int. Ed. 2003, 42, 5513.
[3] M. Back, R. Marin, M. Franceschini, N. S. Hancha, F. Enrichi, E. Travea, S. Polizzi, J. Mater. Chem. C 2016, 4, 1906.
[4] J. T. Van Wijngaarden, S. Scheidelar, T. J. H. Vlugt, M. F. Reid, A. Meijerink, Phys. Rev. B 2010, 81, 15112.
[5] J. Pisarska, A. Kos, W. A. Pisarski, Spectrochim. Acta, Part A 2014, 129, 649.
[6] H. Lin, E. Y. B. Pun, X. Wang, X. Liu, J. Alloys Compd. 2005, 390, 197.
[7] Z. Wang, P. Li, Z. Yang, Q. Guo, J. Lumin. 2014, 151, 170.
[8] X. Min, Z. Huang, M. Fang, Y. Liu, C. Tang, X. Wu, Inorg. Chem. 2013, 52, 6060.
[9] M. Xing, W. Cao, H. Zhong, Y. Zhang, X. Luo, Y. Fu, W. Feng, T. Pang, X. Yang, J. Alloys Compd. 2011, 509, 5725.
[10] L. Guo, Y. Wang, J. Zhang, Y. Wang, P. Dong, Nanoscale Res. Lett. 2012, 7, 636.
[11] J. D. L. Dutra, N. B. D. Lima, R. O. Freire, A. M. Simas, Sci. Rep. 2015, 5, 13695.
[12] D. M. Moran, P. S. May, F. S. Richardson, Chem. Phys. 1994, 186, 77.
[13] Y. Liu, G. Qian, Z. Wang, M. Wang, Appl. Phys. Lett. 2005, 86, 071907.
[14] X. Wang, X. Wang, X. Zheng, L. Zhang, J. Alloys Compd. 2015, 632, 269.
[15] M. Runowski, A. Shiychuk, A. Tymiritski, T. Grzyb, V. Lavrin, S. Lis, ACS Appl. Mater. Interfaces 2018, 10, 17269.
[16] M. O. Rodrigues, J. D. L. Dutra, L. A. O. Nunes, G. F. de Sá, W. M. de Azevedo, P. Silva, F. A. A. Paz, R. O. Freire, S. A. Júnior, J. Phys. Chem. C 2012, 116, 19951.
[17] M. T. Berry, P. S. May, Q. Hu, J. Lumin. 1997, 71, 269.
[18] K. Sawada, T. Nanakura, S. Adachi, J. Alloys Compd. 2016, 678, 448.
[19] L. Wang, Z. Yang, Y. Li, R. Yang, Z. Dai, S. Hu, L. Sun, Y. Tong, Spectrochim. Acta, Part A 2018, 202, 76.
[20] P. A. Tanner, L. Zhou, C. Duan, K.-L. Wong, Chem. Soc. Rev. 2018, 47, 5234.
[21] I. Carrasco, F. Piccinelli, I. Romet, V. Nagirnyi, M. Bettinelli, J. Phys. Chem. C 2018, 122, 6858.
[22] I. Carrasco, F. Piccinelli, M. Bettinelli, J. Phys. Chem. C 2017, 121, 16943.
[23] G. Blasse, Prog. Solid State Chem. 1988, 18, 79.
[24] H. Dornauf, J. Heber, J. Lumin. 1980, 22, 1.
[25] F. K. Fong, D. J. Diestler, J. Chem. Phys. 1972, 56, 2875.
[26] V. Lupei, J. Lumin. 1991, 48, 157.
[27] M. Bettinelli, C. D. Flint, J. Phys.: Condens. Matter 1990, 2, 8417.
[28] M. Bettinelli, C. D. Flint, J. Phys.: Condens. Matter 1990, 2, 8417.
[29] Y. Ruan, Q. Xiao, W. Luo, R. Li, X. Chen, Nanotechnology 2011, 22, 275701.
[30] R. Komban, K. Koempe, M. Haase, Cryst. Growth Des. 2011, 11, 1033.
[31] K. Riwozki, H. Meyssamy, A. Kornowski, M. Haase, J. Phys. Chem. B 2000, 104, 2824.
[32] W. M. Yen, R. M. Selzer, Laser Spectroscopy of Solids, 2nd ed., Springer-Verlag, Berlin 1986, Ch. 3.
[33] D. L. Huber, Phys. Rev. B 1979, 20, 2307.
[34] M. Inokuti, F. Hirayama, J. Chem. Phys. 1965, 43, 1978.
[35] F. T. Rabouw, S. A. den Hartog, T. Senden, A. Meijerink, Nat. Commun. 2014, 5, 3610.
[36] D. Yu, F. T. Rabouw, W. Q. Boon, T. Kieboom, S. Ye, Q. Zhang, A. Meijerink, Phys. Rev. B 2014, 90, 165126.
[37] M. Yokota, O. Taminoto, J. Phys. Soc. Jpn. 1967, 22, 779.
[38] I. R. Martín, V. D. Rodríguez, U. R. Rodríguez-Mendoza, V. Lavín, E. Monroya, D. Jáque, J. Chem. Phys. 1999, 111, 1191.
[39] A. I. Burshtein, Sov. Phys. - JETP 1972, 35, 882.
[40] K. B. Eisenhal, S. Siegel, J. Chem. Phys. 1964, 41, 652.
[41] H. Siebold, J. Heber, J. Lumin. 1981, 22, 297.
[42] D. F. Mullica, D. A. Grossie, L. A. Boatner, Inorg. Chim. Acta 1985, 109, 105.
[43] W. O. Milligan, D. F. Mullica, G. W. Beall, L. A. Boatner, Inorg. Chim. Acta 1983, 70, 133.
[44] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part A, 5th ed., Wiley, New York 1997.
[45] W. Di, X. Wang, P. Zhu, B. Chen, J. Solid State Chem. 2007, 180, 467.
[46] J. J. H. A. van Hest, G. A. Blab, H. C. Gerritsen, C. de Mello Donega, A. Meijerink, J. Phys. Chem. C 2017, 121, 19373.
[47] N. J. Johnson, S. He, S. Xiao, E. M. Chan, H. Dai, A. Almutairi, J. Am. Chem. Soc. 2017, 139, 3275.
[48] M. Chua, P. A. Tanner, J. Lumin. 1995, 66, 203.
[49] J. Dexpert-Ghys, R. Mauricot, M. D. Faucher, J. Lumin. 1996, 69, 203.
[50] M. Bettinelli, F. Piccinelli, A. Speghini, J. Ueda, S. Tanabe, J. Lumin. 2012, 132, 27.
[51] Z. Yahiaoui, M. A. Hassairi, M. Dammak, E. Cavalli, F. Mezzadri, J. Lumin. 2018, 194, 96.
[52] T. K. Anh, T. Ngoc, P. T. Nga, P. Long, W. Strek, J. Lumin. 1988, 39, 215.