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# Mechanism for energy transfer processes between Ce$^{3+}$ and Tb$^{3+}$ in LaPO$_4$:Ce,Tb nanocrystals by time-resolved luminescence spectroscopy

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The energy transfer mechanisms between Ce$^{3+}$ and Tb$^{3+}$ in LaPO$_4$:Ce,Tb nanocrystals have been studied by means of time-resolved luminescence spectroscopy in a wide temperature range (10–300 K). Special attention was paid to detailed comparative analysis of both rise and decay emission components of both Ce$^{3+}$ and Tb$^{3+}$. Surprisingly, a relatively slow rise (several microseconds) of Tb$^{3+}$ emission under 266-nm laser excitation was detected, which corresponds to the 4f–5d transition of Ce$^{3+}$ in LaPO$_4$. It was shown that this rise of Tb$^{3+}$ emission could not have arisen due to relaxation of Ce$^{3+}$ ions, whose excited state has a lifetime of about 20 ns. It was demonstrated that the generally accepted concept of a resonant energy transfer from Ce$^{3+}$ to Tb$^{3+}$ in LaPO$_4$ could not explain the time-resolved luminescence characteristics as well as the observed temperature dependence. Hence, a new concept of the energy transfer process from Ce$^{3+}$ to Tb$^{3+}$ in LaPO$_4$ via host lattice states was suggested and elucidated by proposing several possible models.

**1 Introduction** Nowadays, mainly inorganic crystals are utilized in mass production of phosphors, scintillators, detectors, etc. However, crystals must be of high quality, and therefore their production is expensive. Moreover, rapidly developing technologies demand new cheap materials with variable luminescent properties. One of the present day actual tasks is the fabrication of relatively cheap nanocrystalline materials (nanopowders) because the luminescence intensity and decay time are dependent on the size of the nanocrystals. Hence, one can expect that nanomaterials might have the requested optical parameters. On the other hand, since nanoscale particles do not show any scattering effect in the visible region, embedding in/on transparent matrices (e.g. glass, plastics) is possible.

With this study we report on the results of time-resolved luminescence characteristics for nanosized LaPO$_4$:Ce,Tb (LPO), which nowadays is one of the most promising highly luminescent phosphors and one of the best candidates for biomedical applications such as fluorescence resonance energy transfer (FRET) assays, biolabelling, optical imaging or phototherapy [1–4]. The luminescence properties of LPO have been investigated for both the bulk solid as well as nanoscale material [5–11]. Under UV excitation of the Ce$^{3+}$ ion, a 4f$^1$ → 4f$^0$5d$^1$ transition occurs. After energy transfer from Ce$^{3+}$ to Tb$^{3+}$ a green Tb$^{3+}$ emission resulting from $^5$D$_4$ → $^7$F$_J$ relaxation takes place. Generally speaking, energy transfer plays a major role in most luminescent and laser processes and the appropriate mechanisms for some double-doped crystalline materials have been perfectly established [12–15]. However, the energy transfer mechanism between Ce$^{3+}$ and Tb$^{3+}$ ions in nanosized LPO is not clear so far. Up to now, a resonant energy transfer from Ce$^{3+}$ to Tb$^{3+}$ was tentatively suggested. On the other hand, in many cases for successful realization of a resonant energy transfer it is necessary that the spectral dependence of the excitability of Tb$^{3+}$ overlap strongly with a Ce$^{3+}$ decay. According to literature data [6, 7], the Ce$^{3+}$ emission band does not overlap with the 4f$^8$ → 4f$^8$ absorption of Tb$^{3+}$ in LPO and, therefore, resonant energy transfer processes seem improbable. In order to clarify the mechanism of energy

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transfer processes in nanosized LPO, a time-resolved luminescence spectroscopy technique was applied in the present study.

**2 Experimental** Luminescence measurements were performed under excitation by the fourth harmonic of a YAG:Nd pulsed laser (CryLas GmbH: excitation wavelength is 266 nm, half width of the excitation pulse is 2 ns, laser power is 12 mW). This excitation corresponds well to the 4f–5d absorption band of $Ce^{3+}$ in LPO. Luminescence signals from the sample were focused on the entrance slit of a grating monochromator (MDR-3: focal length is 400 mm, dispersion is 1.3 nm/mm, wavelength range is 200–650 nm, resolution is 1.1 nm) and detected subsequently using a Hamamatsu photomultiplier (H8259). Luminescence decay kinetics was recorded by means of photon counting techniques using a 4-GHz multiscaler (P7887 FAST, ComTec GmbH). Time resolution of the set-up was 1 ns. Luminescence decay kinetics was analysed and a commercial SPECTRA-SOLVE program was used for the deconvolution procedure. Nanopowders were slightly pressed into stainless steel cells and mounted on a cold finger of a closed cycle cryostat (Cryogenics Inc.); luminescence characteristics were studied in the 10–400 K temperature range.

In the present study, LPO (45 mol% of $Ce^{3+}$, 15 mol% of $Tb^{3+}$) nanopowder was produced via a microwave-accelerated synthesis in ionic liquids. This method as well as peculiarities of LPO nanophosphor was described in detail elsewhere [9–11]. The crystallinity of as-prepared LPO is proven by the powder X-ray diffraction (PXRD) pattern (Fig. 1) as well as by high-resolution transmission electron microscopy (HRTEM). Both types of method – as expected – indicate the nanoparticles to crystallize with the monazite type of structure. With the assumption of spherical particles, a mean particle diameter of 8–10 nm is calculated using Scherrer's equation. This value agrees with that determined by electron microscopy [9]. The dopant concentrations of
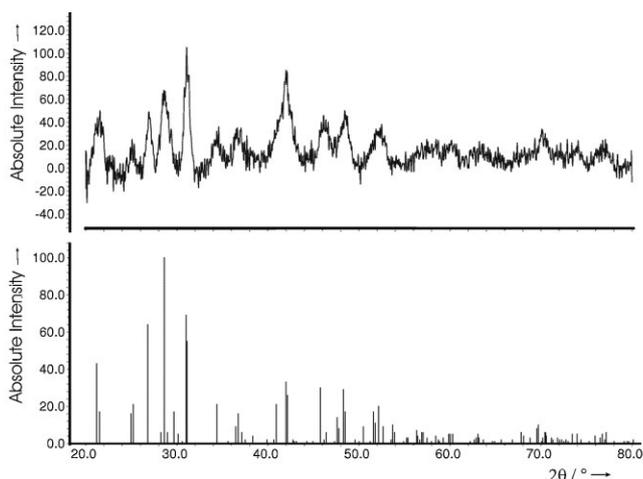
45 mol% $Ce^{3+}$ and 15 mol% $Tb^{3+}$ are quite common for LPO phosphors. Due to the similar radii of the trivalent rare earth ions, phase separation does not occur [14, 15]. The composition and the amount of dopants are confirmed by energy-dispersive X-ray (EDX) analysis. Pressed pellets of the as-prepared nanopowder show values of 39(1) mol% La (expected 40 mol%), 46(1) mol% Ce (expected 45 mol%), and 15(1) mol% Tb (expected 15 mol%).

**3 Results and discussion** The emission spectrum of LPO under 266-nm excitation at room temperature is shown in Fig. 2a. The spectrum consists of two main well-distinguished parts: a broad $4f^1 \rightarrow 4f^05d^1$ $Ce^{3+}$ emission band peaking at $\sim$350 nm and sharp $Tb^{3+}$ lines in the green to red spectral range. The luminescence spectrum observed is in good agreement with literature data [5–11]. We have also measured decay kinetics for both $Ce^{3+}$ and $Tb^{3+}$ emissions. The decay kinetics of $Ce^{3+}$ emission at room temperature is shown in semi-logarithmic scale in Fig. 2b. It is known that the 5d–4f transition in $Ce^{3+}$ is allowed and therefore it decays relatively fast, i.e. it lies in the nanosecond time range. It is clearly seen that the decay curve of $Ce^{3+}$ emission does not obey a single-exponential law; however, it can be approximated by the sum of two exponents with characteristic times of $\sim$4–5 ns ('fast' component) and 15–20 ns ('slow' one). However, it is well known that $Ce^{3+}$ emission in macroscopic $LaPO_4$:$Ce^{3+}$ is exponential with a characteristic time of about 16–18 ns [16]. On the other hand, the decay kinetics of $Ce^{3+}$ emission in nanosized $LaPO_4$:$Ce^{3+}$ is very close to the kinetics depicted in Fig. 2b. It is necessary to note that, generally speaking, energy transfer from $Ce^{3+}$ to $Tb^{3+}$ should influence the decay kinetics of $Ce^{3+}$ emission. However, comparing our $Ce^{3+}$ kinetics with that obtained for nanosized $LaPO_4$:$Ce^{3+}$ [16], we did not see any principal difference. It means that energy transfer from $Ce^{3+}$ to $Tb^{3+}$ does not change the decay kinetics of $Ce^{3+}$ emission. This fact is in principle understandable because radiative transition in $Ce^{3+}$ is already allowed and it cannot be shorter due to energy transfer to $Tb^{3+}$. On the other hand, the intensity of $Ce^{3+}$ emission is much weaker in LPO than in $LaPO_4$:$Ce^{3+}$. We suggest that energy transfer from $Ce^{3+}$ to $Tb^{3+}$ ions leads to the intensity suppression of $Ce^{3+}$ emission in LPO but not to the changes in $Ce^{3+}$ decay kinetics.

The deviations from an exponential law of $Ce^{3+}$ emission decay in nanomaterials have been also observed recently in some other nanocrystalline materials [17–20]. In other words, an additional fast component of $Ce^{3+}$ emission decay (which is absent in single crystals) appears in nanocrystalline materials. From this point of view the decay kinetics of $Ce^{3+}$ in LPO nanopowders is not unique. Several possible origins of this fast component will be discussed below.

In contrast to the allowed d–f transition of cerium, $Tb^{3+}$ f–f transitions are spin and parity forbidden and therefore very long $Tb^{3+}$ luminescence decay (in the millisecond time range) was observed (Fig. 2c). The $Tb^{3+}$ luminescence decay curve shows a double-exponential fit with time constants of
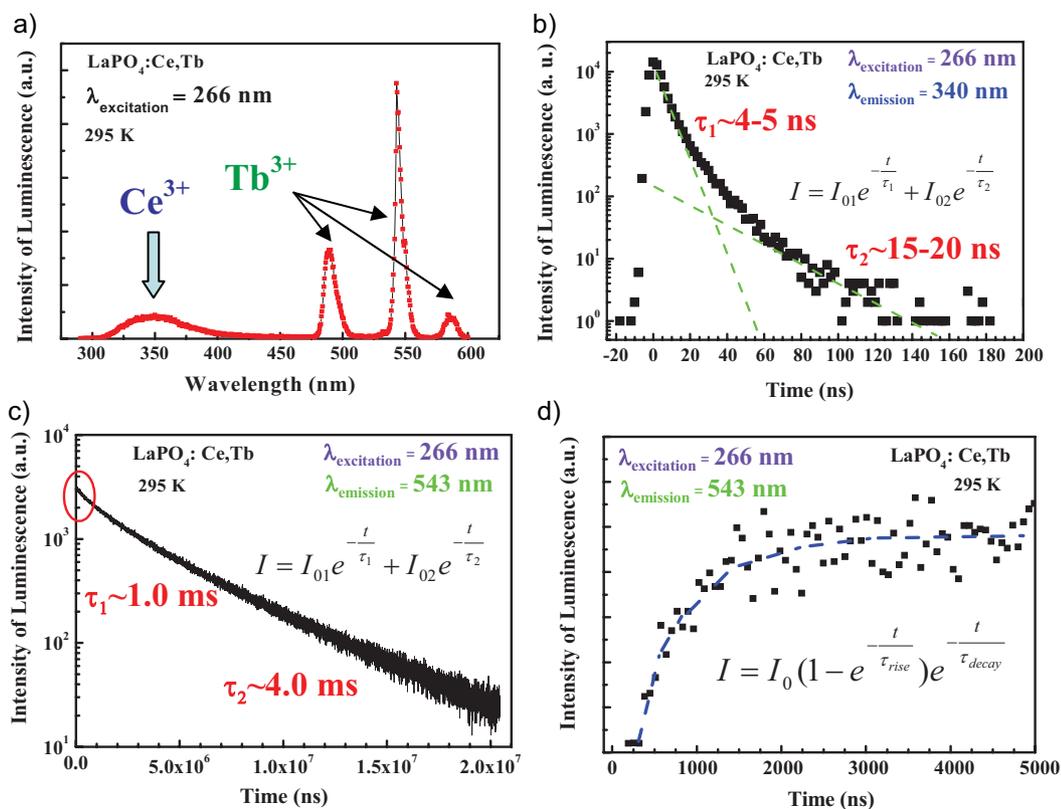


**Figure 1** PXRD pattern of the as-prepared $LaPO_4$:Ce,Tb nanocrystals (top) and the reference pattern for $LaPO_4$ (bottom; JCPDS file no. 84-600).

**Figure 2** (online colour at: www.pss-b.com) Emission spectrum of $LaPO_4$:Ce,Tb nanopowders at room temperature under excitation in 4f–5d absorption band of $Ce^{3+}$ ion (266 nm) (a). Spectral range of the set-up is limited at 600 nm by the grating of the monochromator. Decay kinetics of $Ce^{3+}$ emission (at 340 nm) (b) and $Tb^{3+}$ emission (at 543 nm) (c) in $LaPO_4$:Ce,Tb nanopowders under excitation in 4f–5d absorption band of $Ce^{3+}$ ion (266 nm) are shown in semi-logarithmic scale. Each emission decay kinetics has been fitted by a double exponential law [(b) and (c)] and each exponential component is illustrated schematically by a dashed line on (b). The initial stage of the $Tb^{3+}$ decay kinetics [marked by the red circle in (c)] is shown separately in (d). This initial stage could be described as the sum of two competing processes as described in Ref. [25].

about ∼1 ms ('fast') and ∼4 ms ('slow'). The last value is similar to the 3.2 ms observed earlier [21] for macroscopic samples, i.e. the deviation from single-exponential decay of $Tb^{3+}$ emission takes place in nanocrystals similar to $Ce^{3+}$ emission decay in nanomaterials as described above. Moreover, similar non-exponential decay was already observed for $Tb^{3+}$ emission in nanosized LPO [7], $CePO_4$:$Tb^{3+}$ [22], and nanosized $LaPO_4$:$Tb^{3+}$ [23]. In other words, for both $Ce^{3+}$ emission (allowed transition) as well as $Tb^{3+}$ emission (forbidden transition) similar time-resolved luminescence features was observed.

In principle, there are several reasons which could led to the deviation of the emission decays from the exponential form which are related to the influence of the nanoparticle's surface. These reasons could be as follows. Firstly, the deviation of single-exponential behaviour can be explained by energy transfer from the excited state of $Ce^{3+}$ or $Tb^{3+}$ ions to some traps. Although the origin of these traps is unknown, one can suppose that some defects on the nanoparticle's surface can be quite effective trap charge carriers. Such a model has been discussed in several papers [7, 22]. Secondly, double-exponential decay can reveal two types of

luminescence centres in nanopowders: 'surface'- and 'bulk'-related ions. If $Ce^{3+}$ (or $Tb^{3+}$) ions are located in the 'bulk' region of the nanoparticle, their positions in the crystal lattice and their local surroundings are similar to the positions and the local surroundings of the impurity ions in the bulk material. Such ions have a decay time constant close to the decay time in the macroscopic material, i.e. such ions are responsible for the 'slow' components of the decay kinetics (15–20 ns for the cerium emission and ∼4 ms for the terbium one). However, dopants in the surface region are strongly perturbed by the surface states. It is important to note that their local symmetry is lower than that in the 'bulk' region. Therefore, the decay kinetics due to 'surface' activators becomes shorter, i.e. the double-exponential decay kinetics observed arises from dopants being in two different regions of the nanoparticle. The last model has been used recently to explain non-exponential decay of some rare earth ion (including $Ce^{3+}$) emission in $Y_3Al_5O_{12}$ (YAG) nanocrystals [18, 24, 25].

We would like to mention here that the complex decay kinetics of luminescence could not be explained by different sizes of nanocrystals by analogy with semi-conductor

nanocrystals [26, 27]. Indeed, in the case of a continuous size distribution of semi-conductor nanocrystals the emission decay kinetics is usually described by means of the so-called stretched exponential decay [26, 27]. However, it is interesting to note that our decay kinetics is described perfectly by the sum of two exponents. If we suppose that the complex kinetics of luminescence is as a result of different sizes of nanocrystals, we should also conclude that our nanocrystals have only two exact sizes. But it is not true – our nanopowder has a continuous size distribution [9].

Besides the study of $Ce^{3+}$ and $Tb^{3+}$ relaxation processes, the initial stage of time evolution for $Ce^{3+}$ and $Tb^{3+}$ emissions has been studied, too. Particular attention was focused on the initial part of the decay kinetics of $Tb^{3+}$ emission, which is depicted in Fig. 2d. It is clearly seen that a considerable rise of the emission intensity takes place after the end of the excitation pulse (the duration of the excitation pulse is about 2 ns). This rise of $Tb^{3+}$ emission is about several microseconds and, therefore, it cannot have arisen from a relaxation of $Ce^{3+}$ ions, which have a lifetime in the excited state of about of 20 ns. Furthermore, as we already mentioned above, according to literature data [6, 7] the absorption of $Tb^{3+}$ overlaps poorly with $Ce^{3+}$ emission in LPO that is exceptional for a resonant energy transfer. Last but not least, the strong temperature dependences of $Ce^{3+}$ and $Tb^{3+}$ emissions are depicted in Fig. 3. Usually, a resonant energy transfer is temperature independent but, in Fig. 3, is clearly seen that at low temperatures the intensity of $Tb^{3+}$ emission falls, whereas the intensity of $Ce^{3+}$ luminescence increases, i.e. it is evident that the energy transfer processes are 'frozen' at low temperatures. Summarizing all these above-mentioned experimental facts, we can conclude that the resonant energy transfer from cerium to terbium ions is improbable for LPO nanocrystals. Therefore, we suggest two models which may explain the slowly rising front of the $Tb^{3+}$ emission (Fig. 2d) as well as the temperature dependence of $Ce^{3+}$ and $Tb^{3+}$ emissions depicted in Fig. 3.
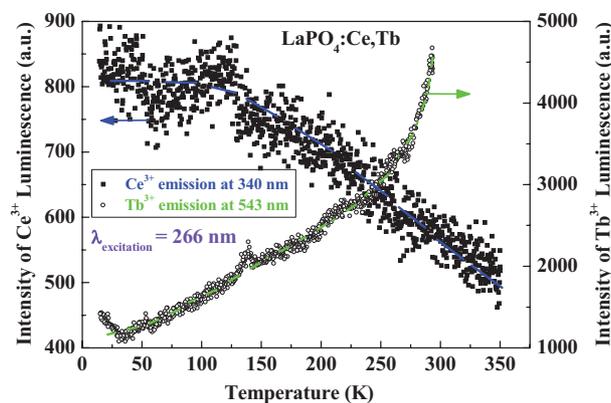
**The model 1** It is obvious that under 266-nm excitation an electron elevated from the ground state to an excited level forms an excited $Ce^{3+}$ centre. After some relaxation the electron from the excited level and the hole from the ground state recombine, emitting a photon. However, if we suppose that the 5d level of $Ce^{3+}$ is located close to the bottom of the conduction band, ionization of $Ce^{3+}$ ions occurs, i.e. the electron transfers from $Ce^{3+}$ to some shallow trap. In this respect, it is necessary to note that such processes are well known and studied in several other materials [28–30]. If the above-mentioned processes occur, then two possible relaxation ways will be realized:

**A.** This model is schematically depicted in Fig. 4a. After ionization of a $Ce^{3+}$ ion, a $Ce^{4+}$ centre will be formed. This centre is unstable; therefore, the excess hole tends to be retrapped by $Tb^{3+}$ ions, i.e. forming $Tb^{4+}$. From literature data it is known that $Tb^{3+}$ is an effective trap for holes [6]. The electron, in turn, can be thermally released from the shallow trap and subsequently trapped by $Tb^{4+}$ forming *excited* $Tb^{3+}$ [denoted as $(Tb^{3+})^*$]. Further relaxation of the excited $Tb^{3+}$ ion leads to terbium-related emission:

$$Tb^{4+} + e^- \rightarrow (Tb^{3+})^* \rightarrow Tb^{3+} + h\upsilon.$$
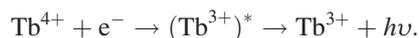
**B.** This model is schematically depicted in Fig. 4b. The hole is localized near the $Tb^{3+}$ ion *without* the formation of $Tb^{4+}$. After liberation of the trapped electron this electron is captured by the localized hole ($h^+$), forming a bound exciton ($e^0$). When deexciting, the exciton transfers its energy to a terbium ion. The $Tb^{3+}$ ion will become excited and subsequently decays under the emission of its characteristic luminescence:

$$Tb^{3+} + h^+ + e^- \rightarrow Tb^{3+} + e^0 \rightarrow (Tb^{3+})^*$$

$$\rightarrow Tb^{3+} + h\upsilon.$$
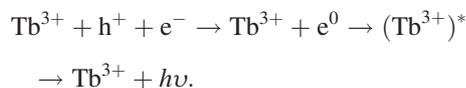
In both the above-mentioned cases a relatively slow rise of $Tb^{3+}$ emission caused by the electron transfer from the trap to the luminescence centre is to be expected. If the temperature of the sample decreases, the probability of the electron's thermal release from the shallow trap decreases, too, and the intensity of $Tb^{3+}$ emission falls at low temperature as shown in Fig. 3.

**The model 2** The excited $Ce^{3+}$ ion can relax, forming a so-called *impurity trapped exciton*. Such relaxation is well known and established for $Er^{3+}$ in semi-conductors [31] as well as in some ionic crystals [32–34]. Slow rise of $Tb^{3+}$ emission could be caused by a slow hopping motion of such an exciton from cerium to terbium ions:

$$(Ce^{3+})^* \rightarrow Ce^{3+} + e^0 \rightarrow Tb^{3+} + e^0 \rightarrow (Tb^{3+})^*$$

$$\rightarrow Tb^{3+} + h\upsilon.$$
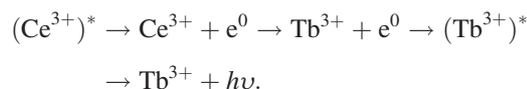
It is necessary to note here that the formation of an impurity *trapped exciton* is possible if the ground level of

**Figure 3** (online colour at: www.pss-b.com) Temperature dependence of $Ce^{3+}$ and $Tb^{3+}$ emissions (at 340 and 543 nm, respectively) in LaPO$_4$:Ce,Tb nanopowders under excitation in 4f–5d absorption band of $Ce^{3+}$ ion (266 nm).
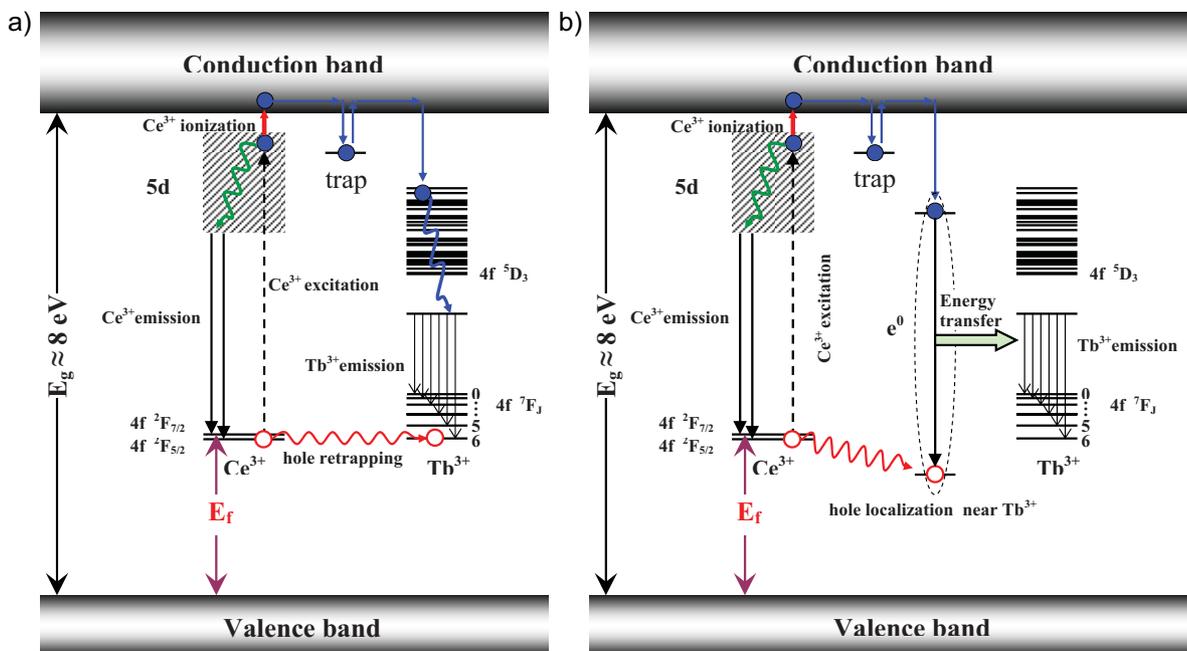
**Figure 4** (online colour at: www.pss-b.com) Energy level scheme of $LaPO_4$:Ce,Tb with optical transitions and energy transfer processes (see details in the text). It is suggested that the 5d levels of the $Ce^{3+}$ ion are located close to the bottom of the conduction band and, therefore, $Ce^{3+}$ ionization processes might occur. After $Ce^{3+}$ ionization a hole is retrapped by a $Tb^{3+}$ ion forming $Tb^{4+}$ (a) or a hole localizes near $Tb^{3+}$ with subsequent formation of a bound exciton $e^0$ (b).

$Ce^{3+}$ is close to the top of the valence band. Unfortunately, there are no reliable data about the position of the ground 4f level of the $Ce^{3+}$ ion in LPO, i.e. the distance between the 4f level of the $Ce^{3+}$ ion and the top of the LPO valence band (denoted as $E_f$ in Fig. 4) is unknown. However, based on the data for other wide band gap oxides, we can conclude that the position of the ground 4f level of $Ce^{3+}$ most likely is quite far from the top of the valence band [35] and therefore the model 2 is quite doubtful. For instance, in YAG the 4f level of $Ce^{3+}$ is located at 3 eV above the valence band [36]. If the ground 4f level is lying at the same distance from the top of the valence band in LPO, too, the first excited 5d level will be just below the bottom of the conduction band and therefore ionization processes (model 1) are quite possible.

Finally, we would like to mention here one more essential detail. All the above-mentioned models imply energy transfer processes via host lattice states. Usually, energy transfer processes via host lattice states are not effective enough due to migrations of charge carriers to some other defects or uncontrolled impurity centres where non-radiative relaxations can take place subsequently. Non-radiative losses during energy transfer via host lattice states could also be suppressed if $Ce^{3+}$ and $Tb^{3+}$ ions are not distributed randomly but form correlated pairs with close distance. Very probably, this is the case realized in doped LPO. That is why the most efficient luminescence has been observed for those LPO samples where the rare earth ion concentration is relatively high: to date, the best concentrations are 45 and 15 mol% for $Ce^{3+}$ and $Tb^{3+}$, respectively [7–11]. Moreover, small particle sizes strengthen the

formation of $Ce^{3+}$ and $Tb^{3+}$ pairs in nanosized samples. It is important to note that both $Ce^{3+}$ and $Tb^{3+}$ replace $La^{3+}$. The ionic radius of $La^{3+}$ in the eightfold coordination is 1.16 Å, while the ionic radii of $Ce^{3+}$ and $Tb^{3+}$ are 1.143 and 1.04 Å [37], respectively. Such quite close values and similar electronic structures provide very favourable conditions for $La^{3+}$ replacement by other $Ln^{3+}$ ions. We have to note also here that the concentrations of both $Ce^{3+}$ and $Tb^{3+}$ are very high and therefore the average distance between impurity ions is estimated as less than two lattice constants. In this case centre-to-centre recombination is predominant, especially in the conditions when recombination between distant ions is not possible due to small nanoparticle size. On the other hand, the small particle size might play a negative role due to charge carrier trapping on the nanoparticle's surface during energy transfer. With respect to the role of surface states in energy transfer processes, we are going to explore core–shell samples because these core–shell samples have different surface states if compared with uncoated ones. This work is in progress and the results will be published in a forthcoming paper.

**4 Conclusions** Time-resolved luminescence of $Ce^{3+}$ and $Tb^{3+}$ ions in nanocrystalline $LaPO_4$ under direct excitation of $Ce^{3+}$ ions has been studied. Special attention was paid to the detailed analysis of the temperature dependence of the luminescence of both $Ce^{3+}$ and $Tb^{3+}$ ions. It was demonstrated that the obtained experimental results could not be successfully described in the framework of resonant energy transfer. Therefore, new

two models of the energy transfer process from $Ce^{3+}$ to $Tb^{3+}$ in $LaPO_4$ via host lattice states were proposed and discussed.

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