Resonant Processes Causing Photon Multiplication in $CaSO_4$:Tb^{3+}

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Abstract

The emission spectra of single and polyterbium centers have been measured at the excitation of $CaSO_4$:Tb^{3+} phosphors with different charge compensators (Na^+, calcium vacancies, etc.) by 3.8–35 eV photons or 5 and 300 keV electrons at 6–300 K. The possible mechanisms providing quantum yield above unity for green ($^5D_4 \rightarrow {}^7F_J$) and blue emission ($^5D_3 \rightarrow {}^7F_J$) of Tb^{3+} at the direct intracenter excitation, excitation of oxyanions or creation of hot (nonrelaxed) electrons and holes have been discussed. On the basis of thermally stimulated luminescence at 6–600 K, the peculiarities of the hopping diffusion of relaxed electrons and holes and their tentative low-temperature self-trapping have been considered.

Keywords: Luminescence; Resonant processes in Tb^{3+} centers; $CaSO_4$

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1. Introduction

Wide-gap materials (E_g = 4–15 eV) doped with di- and trivalent rare earth (RE^{2+} and RE^{3+}) ions are widely used for various technical applications. The complex energy level structure of lanthanides has been thoroughly studied over a long period (see, e.g., El'yashevich, 1961; Dieke, 1968; Van der Kolk et al., 2001; Lakshmanan et al., 2006, 2007; Bos et al., 2008;). The goal of the present paper is to consider briefly the mechanisms providing an efficient impurity luminescence of simple and complex Tb^{3+} centers at the excitation of calcium sulfate (anhydrite) phosphors by photons from 4 to 40 eV or keV-electrons in a wide temperature region starting from 6 K. Particular attention has been given to the processes allowing to obtain photoluminescence with quantum yield QY > 1 for Tb^{3+} complex luminescence centers involving Na^+ ($Na|_{Ca}$), F^- interstitials (F_i^-) or cation vacancies ($V|_{Ca}$) as charge compensators at the direct (intracenter) excitation of Tb^{3+}; at the excitation of oxyanions or at the creation of electron-hole (*e-h*) pairs in $CaSO_4:Tb^{3+}$. The latter case of QY > 1 connected with the multiplication of *e-h* pairs was revealed long ago in doped alkali halide crystals (Ilmas et al., 1965) and investigated later in many binary wide-gap metal oxides (Lushchik et al., 2000). Recently, considerable attention has been focused on the processes of photon cutting and intracenter cascade impurity emission (see, e.g., Van der Kolk et al., 2001; Lee, 2006). The present paper is a continuation of our experimental cycle (Kuryavtseva et al., 2009; 2012; Lushchik et al, 2011) devoted to different excitation mechanisms of Tb^{3+}, Gd^{3+} and Dy^{3+} center luminescence in $CaSO_4$.

2. Experimental

A set of $CaSO_4:RE^{3+}$ (Tb^{3+} or Gd^{3+}) phosphors was synthesized by the solid-state reaction route at the Institute of Physics (Tartu) with regard to the data on crystallization and phase stability of $CaSO_4$ (Freyer and Voigt, 2003). The synthesis procedure of $CaSO_4:Tb^{3+},Na^+$ phosphors is similar to that described by Lakshmanan et al. (2006, 2007). $CaSO_4$ (99.993), $(NH_4)_2SO_4$ (99.999) and TbF_3 (99.99) or GdF_3 (99.99) starting materials were used for the synthesis of phosphors with F_i^- (similar to $CaF_2:RE^{3+}$) or $V|_{Ca}$ as charge compensators, while Tb_4O_7 (99.9) and NaCl (ultra-pure) were used for doping with Tb^{3+} and Na^+. The phosphors were sintered in a reactor with an extra dry air atmosphere at 750°C. The concentration of Tb^{3+} in our phosphors varies from 0.04 to 4%.

The main photoluminescence (PL) experiments were carried out at the SUPERLUMI station of HASYLAB at DESY, Hamburg (Zimmerer, 2007). The excitation spectra were normalized to equal the quantum intensities of the synchrotron radiation (3.8–35 eV) falling onto the crystal. The emission spectra of Tb^{3+}-related centers were recorded by a liquid nitrogen cooled CCD detector. The spectra of cathodoluminescence (CL) were measured in the region of 1.6–11 eV (through double monochromators) at the excitation by an electron gun (2–15 keV, 100–300 nA and 2-mm^2 spot) at 6–420 K. After the electron irradiation was stopped, it was possible to register the spectra of phosphorescence at 6 K and the thermally stimulated luminescence (TSL) at 6–420 K for an integral signal or a certain monochromator-selected emission (heating rate of $\beta = 10$ K min^{-1}).

3. Experimental results and discussion

An ionic-covalent $CaSO_4$ compound (anhydrite) has an orthorhombic (dipiramidal) crystal structure with 24 atoms per unit cell. Each S^{6+} ion is located at the center of a tetrahedron formed by 4 oxygen ions. A Ca^{2+} cation is surrounded by eight O^{2-} ions located in two different positions – O1 and O2. Recently, Pishtshev and Klopov (2012) calculated a $CaSO_4$ cluster (100 atoms) having regard to a Ca^{2+} cation with $[Ar]4s^2 + 3d^0$ valence electron configuration and a vibronic mixing of the proper electronic states (dynamic hybridization) that generates dynamical charge transfer processes. As a result, the theoretical value of E_g = 9.8 eV is very close to the experimental one determined via the excitation spectra of recombination TSL in $CaSO_4$:Tb^{3+},Na^+ (Kudryavtseva et al., 2009; 2012).

The emission spectrum of Tb^{3+} ions contains two series of $4f^8 \to 4f^8$ transitions: the green series (GS) is connected with $^5D_4 \to {}^7F_J$ ($J = 6,5,4,3,2,1$) and the blue one (BS) with $^5D_3 \to {}^7F_J$ transitions. The most intense emission lines correspond to $^5D_4 \to {}^7F_5$, (2.27 eV) and $^5D_3 \to {}^7F_5$ (3.02 eV) transitions. Fig. 1 shows the excitation spectra for the GS and BS emissions of Tb^{3+} measured in $CaSO_4$:Tb^{3+} phosphors with different charge compensators (Na^+ or F^-) using synchrotron radiation of 5–35 eV at 10 K. The spectra contain several regions: $4f^8 \to 4f^7 5d^1$ transitions (~5.8–5.9 eV), excitation of $(SO_4)^{2-}$ oxyanions (8–9 eV) and interband transitions when an exciting photon of $h\nu > 9.5$ eV forms separately an electron and a hole or even two e–h pairs ($h\nu > 23$ eV). In the case of $f \to d$ intracenter excitation, the efficiencies of GS and BS are close at a low concentration of Tb^{3+} (0.04%), while with the rise of impurity concentration above 0.2% GS becomes dominant, $I(GS) > I(BS)$ (see Fig. 1). Such inequality is typical of the overwhelming majority of neutral two-terbium centers ($Tb^{3+}Na^+Tb^{3+}Na^+$ or $Tb^{3+}V|_{Ca}Tb^{3+}$). The first type of two-terbium centers in spectral transformers of VUV-light into a visible one was investigated by Lakshmanan et al. (2006,

2007) and Lushchik et al. (2011). In materials for personal dosimetry (e.g., $CaSO_4$:Dy), the centers involving cation vacancy, detected by a direct EPR method (Bartolin and Onori, 2005 and references therein), are used for prolonged information storage. In $CaSO_4:Tb^{3+},F^{-}$, the presence of $V|_{Ca}$ was experimentally detected as well (Kudryavtseva et al., 2012). The efficiency of GS at the direct excitation of Tb^{3+} centers by the 5.9-eV photons is higher than that at the excitation of oxyanions, $\eta(5.9\ eV) > \eta(8.4\ eV)$, even in $CaSO_4:Tb^{3+},Na^{+}$ with low impurity concentration (0.2%, see Fig. 1*a*). Such inequality is valid at high Tb-Na concentrations and in $CaSO_4:Tb^{3+},F^{-}$ phosphors (Fig. 1*b*) as well. In $CaSO_4:Tb^{3+}(4\%),Na^{+}$, $\eta(\sim 5.9\ eV)$ undoubtedly exceeds unity for GS (see also Lushchik et al., 2011).

The excitation mechanism of impurity PL at $h\nu > E_g$ differs from that at the intracenter excitation. BS is efficient in CL due to the trapping of hot (nonrelaxed) radiation-induced holes by Tb^{3+} and a subsequent recombination of hot *e* with the trapped *h* providing the excitation of Tb^{3+} centers mainly up to the higher $^5D_3$ level. According to Fig. 1, $I(BS) > I(GS)$ in the whole region of $h\nu$ = 11.5–29 eV. One exciting photon of $h\nu$ = 23–30 eV causes the formation of two *e-h* pairs (multiplication process via resonant Auger transitions) resulting in a doubling of η for BS. A decrease of I(BS) at 30–35 eV in $CaSO_4:Tb^{3+},Na^{+}$ is partly caused by an absorption of Na^{+} ions in this region.

Fig. 2 presents a fine structure of the PL line connected with the $^5D_4 \rightarrow {}^7F_5$ electron transitions for two $CaSO_4:Tb^{3+},F^{-}$ phosphors with a different concentration of Tb^{3+} measured at 9 K. A fine structure is different for the case of direct intracenter excitation by the 5.9-eV photons and 16.7-eV photons creating hot *e* and *h*. A prolonged (~30 min) irradiation of phosphors with 5-keV electrons at 6 K causes a significant weakening of a long-wavelengths region of the PL line (see also Kudryavtseva et al., 2009). So, at least two types of centers are responsible for the $^5D_4 \rightarrow {}^7F_5$ emission line. In our opinion, $Tb^{3+}V|_{Ca}Tb^{3+}$ centers can be partly bleached by an electron irradiation. Just these centers serve as efficient traps for the hot *h* formed during irradiation, and the radiation defects – for instance, $(SO_3)^{-}$ (Bortolin and Onori, 2005) – are created at a subsequent recombination of *e* with the trapped *h*.

Fig. 3 demonstrates the energy-level diagram of a single (*a*) and a complex (*b*) terbium center in $CaSO_4$ doped with Tb^{3+}, the charge compensation of which is performed by Na^{+} substituting for Ca^{2+}. The excitation of $Tb^{3+}Na^{+}$ single centers (concentration of ~0.04%) by 3.2–3.4 eV photons results only in the BS emission ($^5D_3 \rightarrow {}^7F_J$) because the energy difference between $^5D_3$ and $^5D_4$ states (~0.8 eV) significantly exceeds the phonon energy and the nonradiative $^5D_3 \rightarrow {}^5D_4$ transitions within a one-terbium center are impossible. However, in a two-terbium center ($Tb^{3+}Na^{+}Tb^{3+}Na^{+}$) there occurs an efficient well-known cross-relaxation process (arrows 2 in Fig. 3*b*): the energy released at the $^5D_3 \rightarrow {}^5D_4$ transition in the first Tb^{3+} ion (A) is used for the excitation of the second Tb^{3+} from the ground $^7F_6$ to $^7F_2$ level. As a result, a GS emission will also arise at the excitation of a two-terbium center.

The GS and BS of Tb^{3+} emission can be also efficiently excited at 5 K in the region of the lowest (with high spin) $4f^8 \rightarrow 4f^7 5d^1$ transitions, which, based on the Dorenbos methodology (2000), are located at ~5.9 eV (Kudryavtseva et al., 2009). It is worth noting that we did not succeed in detecting the $4f^7 5d^1 \rightarrow 4f^8$ ($^7F_6$) emission in the spectral region of 5.6–11 eV using a double VUV monochromator, although GS and BS are clearly observed in the spectra of CL at 6 K. So, nonradiative resonant cooperative transitions are expected in two- and three-terbium centers (polyterbium centers dominate at the impurity concentration of 0.2–4%) at $CaSO_4$:Tb^{3+},Na^{+} excitation by the ~5.9-eV photons (see also Lushchik et al., 2011). Because of the first cooperative transitions (arrows 1 in Fig. 3*b*), the Tb^{3+} (A) ion, excited up to the $4f^7 5d^1$ level, undergoes transition down to the $^5D_3$ level, while the released energy is used for the excitation of the ion B from the ground $^7F_6$ to $^5D_4$ level. The second resonant transition (arrows 2) provides the $^5D_3 \rightarrow {}^5D_4$ transition in the (A) Tb^{3+} ion, while the third (C) terbium ion becomes excited up to the $^7F_2$ level. As a result, one 5.9-eV exciting photon in a triple terbium center leads to the emission of two quanta of green emission (ions B and A).

An analysis of the luminescence kinetics of this process has been performed in the region of 10^{-9} to 10^{-2} s for a set of $CaSO_4$:Tb^{3+} phosphors with different impurity concentration at 80–300 K. It turns out that the considered (1) and (2) cooperative resonant transitions can be tentatively realized in a two-terbium center as well. The first resonant transition (1) causes the attenuation of BS and a fast (~10^{-8} s) rise of the GS emission of Tb^{3+} to be followed by slow decay stages (in a micro- and millisecond range) in the kinetics of the $f \rightarrow f$ emission ($^5D_4 \rightarrow {}^7F_J$ and $^5D_3 \rightarrow {}^7F_J$) in a complex Tb^{3+} center at the excitation of $CaSO_4$:Tb^{3+},Na^{+} by single 3-ns electron pulses from the Koval'chyk-Mesyats type generator (300 keV, repetition period 30 s). As an example, Fig. 4 presents the Tb^{3+} luminescence decay curves at the excitation of $CaSO_4$:Tb^{3+}(1%),Na^{+} with single electron pulses at 80 K (*a*) or the 5.9-eV photons from the Xe-discharge lamp (1 μs) at 295 K (*b*). There are two rise components – in a nano- (not seen in the figure) and microsecond range, and at least two decay components in a micro-millisecond range for GS emission. One of the slow decay components (~600 μs) for BG emission following the ns-rise component coincides with a slow rise component for the GS emission. A detailed analysis of the data on Tb^{3+}-emission decay kinetics will be presented in a separate paper.

The intensity of the CL of Tb^{3+} centers decreases by 30–40% at a cooling of $CaSO_4$:Tb^{3+},Na^+ from 180 to 50 K, and then stays approximately constant down to 6 K. After a relatively weak electron irradiation (5 keV, ~100 nA, 6 K) was stopped, the intensity of Tb^{3+} emission decreased by three orders of magnitude in ten seconds and weakened by a factor of 10 within the following 10 minutes, while the BS of Tb^{3+} emission dominates in the slowly damping tunnel phosphorescence. At a further phosphor heating up to 430 K with $\beta = 10$ K min^{-1}, the TSL was measured above a pedestal of a tunnel phosphorescence.

Fig. 5 shows the TSL curves measured for $CaSO_4$:Tb^{3+},Na^+ $CaSO_4$:Tb^{3+},F^- and $CaSO_4$:Gd^{3+},F^- phosphors. In $CaSO_4$:Tb^{3+}(1%),F^-, there are intense peaks at 58 and 400 K as well as a clearly defined hole-type TSL peak at 313 K. The emission spectrum of the ~58 K TSL peak measured using a CCD detector (see inset) contains the GS and BS of Tb^{3+} emission, suggesting that both single and two-terbium luminescence centers, which provide BS and GS, respectively, are present in the phosphor. Two-terbium $Tb^{3+}V|_{Ca}Tb^{3+}$ centers serve as traps for radiation-induced holes. The recombination of mobile hot *e* with these trapped *h* during an electron irradiation (i.e. in CL) or at unfreezing of the hopping diffusion of self-trapped *e* above 50 K (TSL peak at ~60 K) provides the appearance of mainly GS ($^5D_4 \rightarrow {}^7F_J$) of Tb^{3+} emission. In $CaSO_4$:Gd^{3+},F^-, the TSL registered for the main emission line (3.97 eV) of Gd^{3+} centers contains the ~60 K peak and the intense peak at 385 K, while there are no peaks at 280–340 K, the intensity of which sharply increases with the rise of $Tb^{3+}Na^+$ concentration from 0.2 to 4% in $CaSO_4$:Tb^{3+},Na^+ (peaks are observed even for 0.04% – see Fig. 5). According to an EPR study (Bortolin et al., 2005), the ~400 K TSL peak in a dosimetric $CaSO_4$:Dy^{3+},F^- is connected with the release of *h* from cation vacancies.

More data are needed to prove the freezing (self-trapping) of holes and their hopping diffusion between neighboring oxygen ions in a regular lattice of $CaSO_4$. In our opinion, the unfreezing of self-trapped holes occurs at 100–130 K and the TSL peaks in this region are detectable even in phosphors with a low concentration of RE^{3+} ions (see Fig. 5). The possibility of self-trapping for *e* and *h* in $CaSO_4$ does not contradict to the theoretical calculation by Pishtshev and Klopov (2012) that considered the mixing of empty *d* states of Ca^{2+} and the states of O^{2-} near the top of a valence band and the bottom of a conduction band. Obviously the self-trapping of *e* and *h* should be verified by further EPR measurements.

4. Conclusions

The present paper is a brief intermediate summary of our experimental results obtained for about 50 synthesized $CaSO_4$ phosphors, with varying concentration of Tb^{3+} impurity ions and different types of charge compensation, and taking into consideration recent theoretical calculations. Besides the well-known cross-relaxation process in two Tb^{3+} ions ($^5D_3 \rightarrow ^5D_4$ and $^7F_6 \rightarrow ^7F_2$ transitions in the first and the second ion, respectively), the novel cooperative resonant transitions within pair or more complex terbium centers ($4f^7 5d^1 \rightarrow ^5D_3$ and $^7\mathrm{F}_6 \rightarrow ^5\mathrm{D}_4$ in two Tb^{3+}, respectively) providing GS of terbium emission with $QY > 1$ have been revealed in $CaSO_4$:Tb^{3+},Na^+ phosphors. A partial freezing of Tb- or Gd-related CL in the region of the ~60 K TSL peak is tentatively caused by self-trapping of conduction *d*-electrons.

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References

Bortolin, E., Onori, S., 2005. Features of EPR dosimetry with $CaSO_4$:Dy phosphor. Appl. Radiat. Isotopes 62, 349–352.

Bos, A.J.J., Dorenbos, P., Bessiere, A., Viana, B., 2008. Lanthanide energy levels in YPO_4. Radiat. Meas. 43, 222–226.

Dexter, D.L., 1957. Possibility of luminescent quantum yields greater than unity. Phys. Rev. 108, 630–633.

Dieke, G.H., 1968. Spectra and energy levels of rare earth ions in crystals, Wiley, New York.

Dorenbos, P., 2000. The 5d level positions of the trivalent lanthanides in inorganic compounds. J. Lumin. 91, 155–176.

El'yashevich, M.A., 1961. Spectra of the Rare Earths, U.S. Atomic Energy Commission Transl. No. 4403, New York.

Freyer, D., Voigt, W., 2003. Crystallization and phase stability of $CaSO_4$ and $CaSO_4$-based salts. Monatsh. Chem. 134, 693–719.

Ilmas, E.R., Liidya, G.G., Lushchik, Ch.B., 1965. Photon multiplication in crystals, I. Opt. Spectrosc. 18, 255–259.

Kudryavtseva, I., Liblik, P., Lushchik, A., Maaroos, A., Vasil'chenko, E., Azmaganbetova, Z., Nurakhmetov, T., Toxanbayev, B., 2009. Electron-hole and excitonic processes in $CaSO_4$ doped with Gd^{3+}, Tb^{3+} and Dy^{3+} luminescent ions. J. Lumin. 129, 1890–1893.

Kudryavtseva, I., Lushchik, A., Maaroos, A., Azmaganbetova, Z., Nurakhmetov, T., Salikhodja, Z., 2012. Recombination luminescence of $CaSO_4$:Tb^{3+} and $CaSO_4$:Gd^{3+} phosphors. Centr. Eur. J. Phys. 10, 995–1001.

Lakshmanan, A., Kim, S.-B., Kum, B.G., Jang, H.M., Kang, B.K., 2006. Rare earth doped $CaSO_4$ luminescence phospors for applications in novel displays – new recipes. Phys. Status Solidi A 203, 565–577.

Lakshmanan, A. R., Kim, S.-B., Jang, H.M., Kum, B.G., Kang, B.K., Heo, S., Seo, D., 2007. A quantum-splitting phosphor exploiting in the energy transfer from anion excitons to Tb^{3+} in $CaSO_4$:Tb,Na. Adv. Functional Materials 17, 212–218.

Lee, T.-J., Luo, L.-Y., Diau, E.W.-G., Chen, T.-M., Cheng, B.-M., Tung, C.-Y., 2006. Visible quantum cutting through downconversion in green-emitting K_2GdF_5:Tb^{3+} phosphors. Appl. Phys. Lett.89, 131121.

Lushchik, A., Kirm, M., Lushchik, Ch., Martinson, I., Zimmerer, G., 2000. Luminescence of free and self-trapped excitons in wide-gap oxides. J. Lumin. 87/89, 232–234.

Lushchik, A., Lushchik, Ch., Kudryavtseva, I., Maaroos, A., Savikhin, F., Shablonin, E., Vasil'chenko, E., 2011. Low-temperature investigation of electronic excitations in wide-gap materials doped with RE^{3+} and Cr^{3+} impurity ions. Opt. Spectrosc. 111, 434–440.

Pishtshev, A., Klopov, M., 2012. A comparative study of structural energetics and chemical bonding in Ca-based dielectric materials: an integratyed view from first-principles, in: Strensbergs, A., Grinberga, L. (Eds.) Abstr. Intern. Conf. on Functional Materials and Nanotechnologies, Riga, p.117.

Van der Kolk, E., Dorenbos, P., Vink, A.P., Perego, R.C., Van Eijk, C.W.E., Lakshman, A.R., 2001. Vacuum ultraviolet excitation and emission properties of Pr^{3+} and Ce^{3+} in *M*SO4 (*M* = Ba, Sr, and Ca) and predicting quantum splitting by Pr^{3+} in oxides and fluorides. Phys. Rev. B 64, 195129.

Zimmerer, G., 2007. SUPERLUMI: A unique setup for luminescence spectroscopy with synchrotron radiation. Radiat. Meas. 42, 859.

Captions

Fig. 1. Excitation spectra measured for the 2.27 eV ($^5D_4 \rightarrow {}^7F_5$, curves 1) or 3.02 eV ($^5D_3 \rightarrow {}^7F_5$, curves 2) emission of Tb^{3+} ions in $CaSO_4:Tb^{3+}$(0.2%),Na^+ (*a*) and $CaSO_4:Tb^{3+}$(1%),F^- (*b*) phosphors at 10 K.

Fig. 2. Fine structure of the $^5D_4 \rightarrow {}^7F_5$ transition for Tb^{3+} centres at the photoexcitation of $CaSO_4:Tb^{3+}$(1%),F^- (curves 1) and $CaSO_4:Tb^{3+}$(4%),F^- (curves 2) phosphors at 9 K.

Fig. 3. Energy-level diagram of a three-terbium luminescence center in $CaSO_4:Tb^{3+}$,Na^+. Intracenter resonant cooperative transitions are indicated by arrows 1 and 2.

Fig. 4. Decay curves of the green (curves 1) and blue emission (curves 2) at the excitation of a $CaSO_4:Tb^{3+}$(1%),Na^+ phosphor with 300-keV electron single pulses at 80 K (*a*) or 5.9 eV photons from the Xe-discharge lamp at 295K (*b*).

Fig. 5. Spectrally integrated TSL curves measured for $CaSO_4:Tb^{3+}$(1%),F^- (curve 1), $CaSO_4:Gd^{3+}$(1%),F^{-144} (2) and $CaSO_4:Tb^{3+}$(0.04%),Na^+ (3) phosphors irradiated by 6-keV electrons at 6 K. $\beta = 10$ K min^{-1}. Inset shows the emission spectrum for the ~60 K TSL peak (from curve 1).

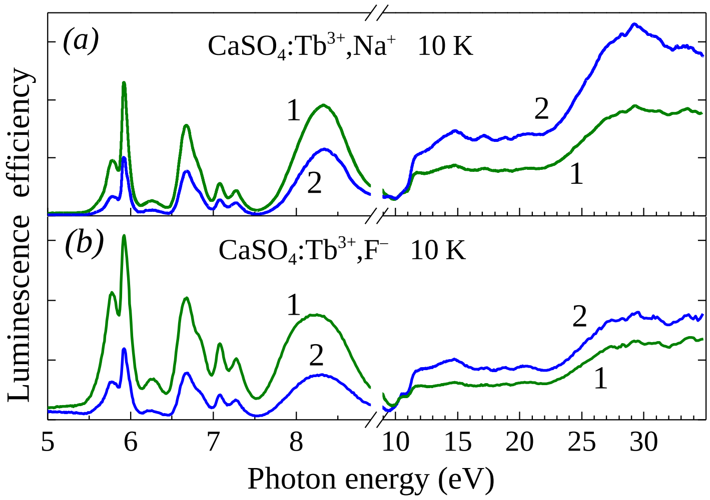

Fig.1

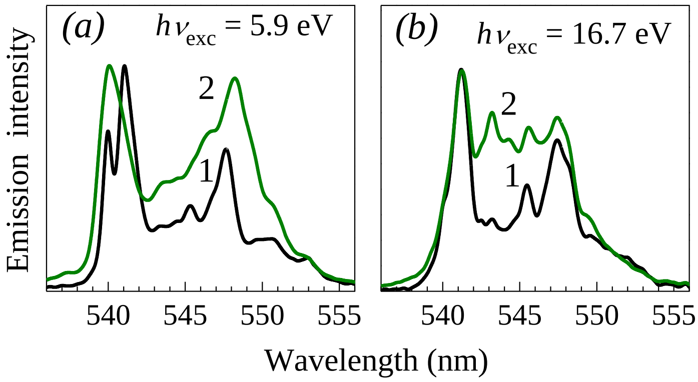

Fig. 2

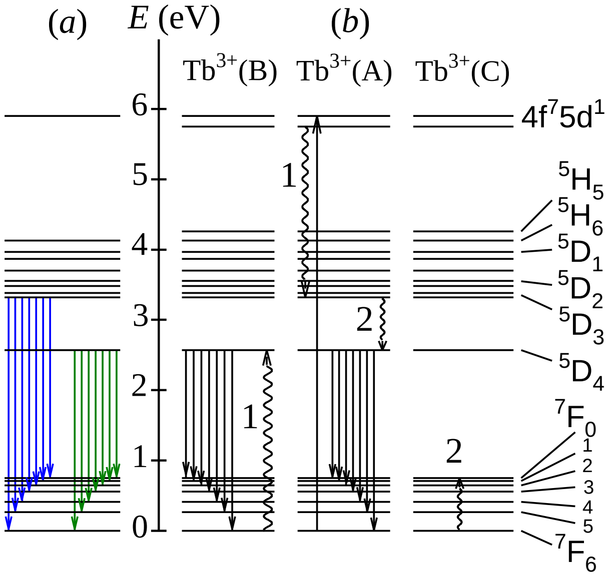

Fig.3

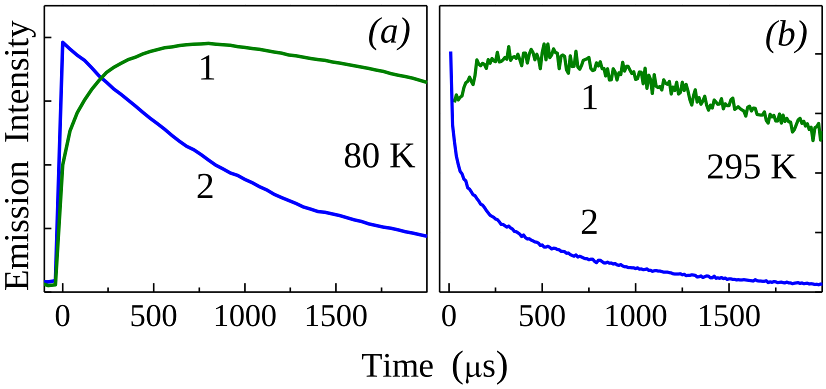
(a)
(b)
Emission Intensity
1
2
80 K
1
2
295 K
0
500
1000
1500
0
500
1000
1500
Time (μs)

Fig.4

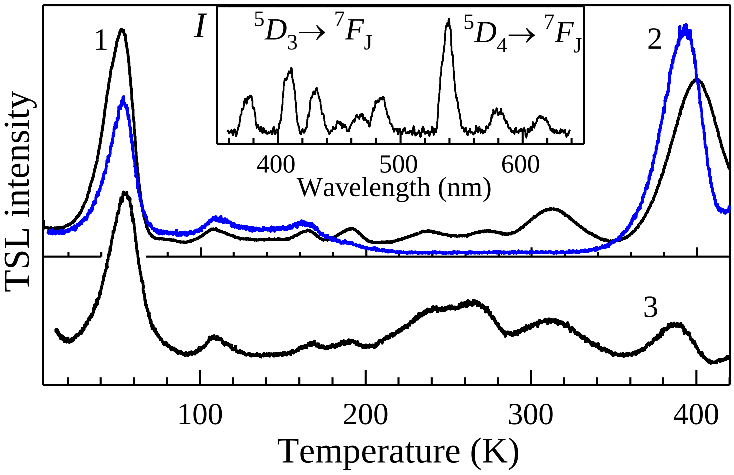
1
I
$^5D_3 \rightarrow {}^7F_J$
$^5D_4 \rightarrow {}^7F_J$
2
400
500
600
Wavelength (nm)
TSL intensity
3
100
200
300
400
Temperature (K)

Fig. 5