Recombination luminescence of $\text{CaSO}_4:\text{Tb}^{3+}$ and $\text{CaSO}_4:\text{Gd}^{3+}$ phosphors*

Research Article

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Abstract:

A comparative study of the excitation of luminescence by VUV radiation as well as of thermally and photo-stimulated luminescence has been carried out for $\text{CaSO}_4:\text{Tb}^{3+}$ and $\text{CaSO}_4:\text{Gd}^{3+}$ phosphors, where Na^+ or F^- ions are used for charge compensation. The distinction in hole processes for the phosphors with Na^+ or F^- compensators is determined by the differing thermal stability of the holes localized at/near $\text{Tb}^{3+}\text{Na}^+$ and $\text{Gd}^{3+}\text{Na}^+$ (up to 100-160 K) or at/near $\text{Tb}^{3+}\text{F}^-V_{\text{Ca}}$ and $\text{Gd}^{3+}\text{F}^-V_{\text{Ca}}$ centers involving also a cation vacancy (up to 400-550 K). Tunnel luminescence in the pairs of localized electrons and holes nearby Tb^{3+} or Gd^{3+} has been detected. The mechanisms of electron-hole, hole-electron and tunnel recombination luminescence as well as a subsequent released energy transfer to RE^{3+} ions are considered.

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1. Introduction

Wide-gap luminescent materials based on calcium sulphates doped with Mn^{2+} and many rare-earth (RE^{3+}) ions have long been in use for the detection of vacuum ultraviolet (VUV) radiation and personal dosimetry. The possibility to use $\text{CaSO}_4:\text{Tb}^{3+}$ [1–3] and $\text{BaSO}_4:\text{Pr}^{3+}$ [4] phosphors as efficient spectral transformers in flu-

orescent tubes is considered also. The functioning of these transformers is based on the phenomena of photon multiplication [5, 6] or photon cutting [7]. In CaSO_4 where the concentration of RE^{3+} can be up to 5–7%, there is a total absorption of the exciting VUV-radiation, which provides either the direct excitation of the $4f^n \rightarrow 4f^{n-1}5d^1$ intracentre transitions or the excitation of oxyanions (SO_4^{2-}) and the formation of separated electrons and holes, with the subsequent energy transfer from the matrix to luminescence impurity centers [see, e.g., 8].

The aim of the present study is to analyze thoroughly the excitation recombination mechanisms of impurity lu-

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minescence in $\text{CaSO}_4:\text{Tb}^{3+}$ and $\text{CaSO}_4:\text{Gd}^{3+}$ phosphors, where the effective charge of RE^{3+} ions substituting for Ca^{2+} cations is compensated by either Na^+ ions [similar to 1, 8] or F^- ions. It has been shown earlier [see, e.g., 9, 10] that at least three different types of recombination impurity luminescence occur in face-centered cubic alkali halide crystals doped with mercury-like s^2 ions (In^+ , Sn^{2+} , Tl^+ , Pb^{2+}): (i) electron recombination luminescence, when conduction electrons (e) recombine with the holes (h) localized at/near impurity centers, (ii) hole recombination luminescence caused by the recombination of mobile holes with the electrons localized at/near impurity ions, and (iii) tunnel luminescence connected with the recombination between localized but spatially close e and h . Recently, tunnel luminescence has been detected in $\text{CaSO}_4:\text{Tb}^{3+}$ irradiated by an electron beam at 6 K [8]. In low-symmetry CaSO_4 crystals X-irradiated at 300 K, the localization of holes in the form of SO_4^- nearby a cation vacancy V_{Ca} has been detected by the electron paramagnetic resonance (EPR) method [11]. It has been suggested that, similar to some other low-symmetry wide gap metal oxides, a self-trapping of holes (formation of SO_4^- oxyanion) is possible in regular regions of CaSO_4 at low temperatures [8].

2. Experimental

An ionic-covalent CaSO_4 compound (anhydrite) has an orthorhombic (dipiramidal) crystal structure, with a unit cell containing 24 atoms and where the parameters $a = 6.993$, $b = 6.995$ and $c = 6.245$ Å [see 12, and references therein]. Each S^{6+} ion is located at the center of a tetrahedron formed by four oxygen ions. A Ca^{2+} cation is surrounded by 8 O^{2-} ions located in two different positions – O1 and O2. X-ray structure analysis and the synthesis procedure of $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$ phosphors is described in detail in [1, 13]. Using this procedure [1], the synthesis of phosphors with varying concentration of Tb^{3+} or Gd^{3+} was carried out at the Institute of Physics (Tartu). Single $\text{Tb}^{3+}\text{Na}^+$ terbium centers dominate in the phosphor with low concentration of Tb^{3+} impurity ions (about 0.2%), while mainly pair terbium centers $\text{Tb}^{3+}\text{Na}^+\text{Tb}^{3+}\text{Na}^+$ and even triplet terbium centers are formed in the phosphors doped with 1% or 4% of terbium, respectively [2, 3]. The amount of Na^+ compensators (added in the form of NaCl) in phosphors exceeds the amount of terbium ions.

For comparison, $\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$ and $\text{CaSO}_4:\text{Gd}^{3+},\text{F}^-$ phosphors, where fluorine ions (5N purity TbF_3 or GdF_3 was added to a CaSO_4 salt) substitute for O^{2-} ions and are used for charge compensation, have been synthesized

as well. A firing has been performed in an air atmosphere at the temperature $T = 1023$ K $\approx 0.6T_{\text{melt}}$ (melting point for CaSO_4 is $T_{\text{melt}} = 1673$ K), which is optimal for solid-state reactions. We have succeeded in preparing fluorine-containing phosphors (firing at 750°C) with Tb^{3+} concentration not higher than 0.3 at%. In the paper we present data only for the phosphors with 1% of RE^{3+} ions added to CaSO_4 salt during the synthesis. So, this concentration of Tb^{3+} or Gd^{3+} impurity ions will not be marked additionally in the further text.

Thermally stimulated luminescence (TSL) drastically differs for $\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$ and $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$ – in F^- -containing phosphors there are no TSL peaks in the region of 250 K, while intense peaks are observed at 460 and 580 K. According to EPR study of $\text{CaSO}_4:\text{Dy}^{3+}$ [11, 14], these high-temperature TSL peaks are connected with a deep hole trap – an O^- ion (in position 1 or 2) that is incorporated into SO_4^- nearby a cation vacancy [V_{Ca}^{2-} (superscript shows an effective charge with respect to a neutral lattice)]. So, in our opinion, the introduction of TbF_3 leads to either charge compensation of $[\text{Tb}_{\text{Ca}}]^+$ or the formation of a small amount of hole trapping centers – $[\text{F}_{\text{O}}V_{\text{Ca}}\text{F}_{\text{O}}]^0$ or $[\text{F}_{\text{O}}V_{\text{Ca}}]^-$.

$\text{CaSO}_4:\text{Gd}^{3+},\text{Na}^+$ phosphors have been synthesized by the above-mentioned procedure. In the case of $\text{CaSO}_4:\text{Gd}^{3+},\text{F}^-$ phosphors, GdF_3 of 5N purity was used. Earlier, the same $\text{CaSO}_4:\text{Gd}^{3+}$ and $\text{CaSO}_4:\text{Tb}^{3+}$ phosphors were investigated at 8 and 300 K [2, 3, 8, 15] using excitation by 2–15 keV electrons [for experimental details see 16] or synchrotron radiation of 4–35 eV at the SUPERLUMI station of HASYLAB at DESY [for details see 17]. A fine structure of the emission spectrum of Tb^{3+} centers was measured using a monochromator-spectrograph SpectraPro-308i equipped with a liquid nitrogen cooled CCD detector [2, 3]. The spectrum contains two series of $4f^8 \rightarrow 4f^8$ radiative transitions of Tb^{3+} ions: $^5D_4 \rightarrow ^7F_1$ ($J = 6,5,4,3,2,1$, the so-called "green" series) and $^5D_3 \rightarrow ^7F_1$ ("blue" series). The most intense emission lines correspond to $^5D_4 \rightarrow ^7F_5$, $^5D_4 \rightarrow ^7F_6$ (2.27 and 2.54 eV) and $^5D_3 \rightarrow ^7F_5$, $^5D_3 \rightarrow ^7F_6$ (3.02 and 3.26 eV) transitions.

The present paper focuses on the excitation spectra for steady-state luminescence, phosphorescence, TSL and photo-stimulated luminescence (PSL) of Tb^{3+} and Gd^{3+} ions measured for four CaSO_4 phosphors (Na^+ or F^- as charge compensators) at 80 K using a hydrogen discharge source of 4–13.5 eV (equal quantum intensities of the exciting radiation were used). The reference signal for normalization was recorded from a sodium salicylate. TSL

was measured at 80–500 K using the same setup and constant heating rate of $\beta = 10 \text{ K min}^{-1}$. Particular attention was paid to PSL still uninvestigated in the four above-mentioned phosphors. After the irradiation by photons of defined energy, a phosphor was stimulated by a light from an incandescent lamp through a double prism monochromator, and the PSL of Gd^{3+} ions (${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions [18]) was selected using an interference filter (313 nm), while a combination of optical filters was used for the registration of green (${}^5D_4 \rightarrow {}^7F_J$, 1.94–2.55 eV) or blue emission (${}^5D_3 \rightarrow {}^7F_J$, 2.55–3.35 eV) of Tb^{3+} ions. The stimulation spectra of PSL were measured at equal quantum intensities of the stimulation light.

3. Experimental results and discussion

Figure 1a demonstrates the excitation spectra for the 3.97 eV emission of Gd^{3+} ions (${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ electron transitions) for a $\text{CaSO}_4:\text{Gd}^{3+},\text{Na}^+$ phosphor at 80 and 430 K. Besides the narrow excitation band at 3.97 eV (practically resonant with Gd^{3+} emission, not shown in the figure), Gd^{3+} emission at 80 K is efficiently excited at the direct excitation of oxyanions (8–9 eV) and in the region of band-to-band transitions, where the photons of $h\nu = 9.5\text{--}11.5$ eV form separated e and h , and excite recombination phosphorescence. The heating of a sample to 430 K causes a sharp thermal quenching of gadolinium emission. However, weak bands at 7.4–8.5 eV (distorted oxyanions) still remain in the excitation spectrum. The Gd^{3+} emission remaining at 430 K is tentatively connected with tunnel recombination of e and h localized near Gd^{3+} (see next Section).

Figure 1b shows the excitation spectra for strictly separated green and blue emissions of Tb^{3+} centers in a $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$ phosphor at 80 and 430 K. A fine structure of the green and blue series of $f\text{--}f$ electron radiative transitions in $\text{Tb}^{3+}\text{Na}^+\text{Tb}^{3+}\text{Na}^+$ pair terbium centers – ${}^5D_4 \rightarrow {}^7F_J$ and ${}^5D_3 \rightarrow {}^7F_J$ ($J = 6,5,4,3,2,1$) have been earlier studied at 9 K [2, 3]. According to Fig. 1b, green emission is efficiently excited at 80 K either in the region of the lowest $4f^8 \rightarrow 4f^75d^1$ transitions (5.7 and 5.9 eV) or at high-energy $f\text{--}d$ transitions [see, e.g., 18]. The ~ 7.8 eV $f\text{--}d$ transition is well-defined in the excitation spectrum at 430 K, when the efficiency of either Tb^{3+} emission at the direct impurity centre excitation or the energy transfer from the excited oxyanions to terbium centers is low. It is worth noting that at 9 K the efficiency of ${}^5D_4 \rightarrow {}^7F_J$ radiative transitions at the direct excitation of Tb^{3+} is several times as high as that of blue emission,

Figure 1. Excitation spectra measured for the 3.97 eV emission of Gd^{3+} ions in $\text{CaSO}_4:\text{Gd}^{3+},\text{Na}^+$ (a) and green (${}^5D_4 \rightarrow {}^7F_J$, curve 1') or blue (${}^5D_3 \rightarrow {}^7F_J$, curves 1 and 2) emissions of Tb^{3+} ions in $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$ (b) at 80 (1, 1') and 430 K (2).

while the contribution of blue emission increases if the exciting photons form separated e and h [2, 3].

$\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$ phosphors where, instead of Na^+ , fluorine ions are used for charge compensation have been synthesized for the first time. It turns out that, in case of fluorine compensator, the concentration of Tb^{3+} in phosphors does not exceed 0.3 at%. Figure 2a presents the excitation spectra measured for the emission lines of Tb^{3+} centers (selected though a monochromator) at 2.27 eV (${}^5D_4 \rightarrow {}^7F_5$) and 3.02 eV (${}^5D_3 \rightarrow {}^7F_5$) in $\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$ using synchrotron radiation of the SUPERLUMI station at 10 K. Because of the low concentration of terbium ions in a $\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$ phosphor, pair Tb^{3+} centers are practically absent and the intensity ratio of blue and green emissions ($I_{\text{blue}}/I_{\text{green}}$) at the direct excitation of single Tb^{3+} via $4f^8 \rightarrow 4f^75d^1$ is significantly higher than that typical of pair $\text{Tb}^{3+}\text{Na}^+\text{Tb}^{3+}\text{Na}^+$ centers (see Fig. 1b). According to our recent results [2, 3], a low efficiency of radiative ${}^5D_3 \rightarrow {}^7F_J$ transitions in pair terbium centers (with respect to the case of single Tb^{3+}) at the excitation by 5.8–6.0 eV photons providing $4f^8 \rightarrow 4f^75d^1$ transitions is caused by the cooperative transitions with the participation of two spatially close Tb^{3+} ; i.e., a resonant transfer

Figure 2. Excitation spectra measured for the 2.27 eV ($^5D_4 \rightarrow ^7F_5$, curve 1) or 3.02 eV ($^5D_3 \rightarrow ^7F_5$, curve 2) emission of Tb^{3+} ions in a $\text{CaSO}_4:\text{Tb}^{3+}, \text{F}^-$ phosphor at 10 K (a) and 300 K (b).

of the energy connected with $^5D_3 \rightarrow ^5D_4$ transition in the first Tb^{3+} to the second Tb^{3+} , thus causing its excitation via the $^7F_6 \rightarrow ^7F_{2,3}$ transition. For the case of single Tb^{3+} centers, the value of $I_{\text{blue}}/I_{\text{green}}$ at the excitation in the region of band-to-band transitions is even higher than at intracentre $f \rightarrow d$ transitions.

The excitation spectra for blue and green emissions in $\text{CaSO}_4:\text{Tb}^{3+}, \text{F}^-$ undergo drastic changes with the rise of temperature from 10 K to 300 K (see Fig. 2b). The efficiency of green emission (2.27 eV) at the excitation in the region of the lowest $4f^8 \rightarrow 4f^75d^1$ transitions (5.7 and 5.9 eV) or oxyanions (8–9 eV) at 300 K is about twice as low as at 10 K. At 300 K, there is a strongly broadened excitation band for green emission at 6.2–7.7 eV. A similar excitation band at 5–8.6 eV is observed for blue emission, but the efficiency of blue emission at 300 K is four times as low as at 10 K. At the same time, the efficiency of blue emission at the excitation by 11–15 eV photons forming separated e and h decreases only by a factor of about 1.5 with the temperature rise from 10 to 300 K, and at room temperature it already exceeds the corresponding values at $h\nu = 5$ –9 eV.

It should be pointed out that the revealed differ-

ences in physical processes for $\text{CaSO}_4:\text{Tb}^{3+}, \text{Na}^+$ and $\text{CaSO}_4:\text{Tb}^{3+}, \text{F}^-$ phosphors at 300 K are not unexpected. It has long been known [13, 19] that the synthesis of dosimetric $\text{CaSO}_4:\text{Dy}^{3+}$ phosphors (TSL at 450–550 K is used for dosimetric purposes) should be performed under conditions that impede the introduction of Li^+ , Na^+ or K^+ ions into the matrix. The charge compensation of Dy^{3+} (about 0.3 at%) in the optimal dosimetric phosphor without fading is accomplished by V_{Ca} [19]. The last fact is confirmed by the EPR study of deep hole traps (O^-) responsible for the appearance of the TSL peaks at 460 and 580 K, via the recombination of becoming mobile h with the electrons still localized at/near Dy^{3+} [11, 14].

Figure 3 shows the TSL curves measured for $\text{CaSO}_4:\text{Tb}^{3+}, \text{F}^-$ and $\text{CaSO}_4:\text{Tb}^{3+}, \text{Na}^+$ phosphors previously irradiated by an equal dose of X-rays at 300 K. The intense high-temperature peaks (heating rate of $\beta = 2.86 \text{ K s}^{-1}$) are detected in $\text{CaSO}_4:\text{Tb}^{3+}, \text{F}^-$, where fluorine ions serve as charge compensators and simultaneously promote the formation of V_{Ca} , which compensate the excess of F^- in the matrix (TbF_3 is added to a CaSO_4 salt). Irradiation of CaSO_4 by X-rays causes the formation of a large number of e and h and the appearance of intense TSL peaks at 430, 460, 500 K, and an especially intense peak at 580 K. Preheating of the irradiated phosphor up to 690 K, rapid cooling down and the second heating allow it to register also the 725 K peak that correlates with the annealing of the EPR signal of SO_3^- radicals in X-irradiated $\text{CaSO}_4:\text{Dy}^{3+}$ [14]. In our opinion, the absence of one of O^{2-} ions from a tetrahedron can be considered as an anion vacancy with a localized electron (an analogue to an F^+ centre in MgO and CaO). As a complementary defect, an interstitial ion O_i^- should be formed as well.

To elucidate the contribution of different types of recombination luminescence, the temperature dependence of phosphorescence (for impurity emission) have been studied in the phosphors previously irradiated by 10.5 eV photons at 80 K, when the existence of stable self-trapped holes in the form of SO_4^- is suggested. Figure 4 demonstrates such temperature dependences for $\text{CaSO}_4:\text{Tb}^{3+}, \text{Na}^+$ and $\text{CaSO}_4:\text{Tb}^{3+}, \text{F}^-$ phosphors. After the irradiation by 10.5 eV photons (region of band-to-band transition) was stopped, a damping phosphorescence (for a Tb^{3+} emission) was registered during the following 5 min (intensity decreases by several times) and then, at a further phosphor heating ($\beta = 10 \text{ K s}^{-1}$), the TSL was measured above a pedestal of tunnel luminescence (TL) which was practically independent of temperature across a wide range of values. The TSL peak at $\sim 110 \text{ K}$ is de-

Figure 3. Spectrally integrated (3.7–1.7 eV) TSL curves measured for $\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$ (curves 1 and 1') and $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$ phosphors (curve 2) previously irradiated by the equal dose of X-rays at 300 K. Curve 1' is measured after the preheating of an irradiated phosphor to 690 K. $\beta = 2.86 \text{ K s}^{-1}$.

tected in both phosphors, while there is no intense TSL at 200–275 K in a fluorine-containing phosphor. After preheating of irradiated $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$ up to 210 K and fast cooling down again to 80 K, the intensity of TL (I_{TL}) sharply decreases and, in contrast to $\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$, a sharply rising TSL is detected at 215–250 K.

A temperature dependence of tunnel luminescence has been measured for phosphors irradiated by 10.5 eV photons at 80 K (see Fig. 4). A phosphor was preheated up to the temperature T_1 , cooled down to $T_0 = 80 \text{ K}$ and, after a 5 min delay, the value of I_{TL} was measured. Thereafter, the sample was preheated to $T_2 > T_1$, cooled down and I_{TL} was again measured at T_0 . In such a manner I_{TL} was measured for a number of preheating temperatures. In $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$, there are two decay stages in the temperature dependence of I_{TL} – the first stage at 120–130 K and the second one at 220–280 K. The analysis of our experimental results allows us to associate the first stage with the release of h and its diffusion toward localized e . The second decay stage of I_{TL} , resulting in practically complete annealing of TL, is connected with the release of the second component of a tunnel pair – an electron – from a trap.

Figure 4b shows similar results for $\text{CaSO}_4:\text{Gd}^{3+},\text{Na}^+$ and $\text{CaSO}_4:\text{Gd}^{3+},\text{F}^-$ phosphor irradiated by 10.5 eV photons at 80 K. The TSL for the 3.97 eV emission of Gd^{3+} ions was measured above a pedestal of TL. The annealing of TL occurs at 100–200 K and is accompanied by two TSL peaks with maxima at ~ 110 and $\sim 155 \text{ K}$. The annealing stage at 180–200 K is tentatively connected with the thermal destruction of an electron Gd^{2+} center

Figure 4. Temperature dependences of phosphorescence for $\text{CaSO}_4:\text{Tb}^{3+},\text{Na}^+$, $\text{CaSO}_4:\text{Tb}^{3+},\text{F}^-$ (a) and $\text{CaSO}_4:\text{Gd}^{3+},\text{Na}^+$, $\text{CaSO}_4:\text{Gd}^{3+},\text{F}^-$ phosphors (b) irradiated by 10.5 eV photons at 80 K. TSL was measured for the blue emission of Tb^{3+} ions (curves 1, 1', 1'', 2) or Gd^{3+} emission (curves 1 and 2). TSL curves 1' and 1'' were measured after the preheating of an irradiated phosphor to 210 K and 290 K, respectively. Temperature dependence of tunnel luminescence (curve 3, see text for details) measured for Tb^{3+} and Gd^{3+} emission. TSL curves are normalized at 80 K. $\beta = 10 \text{ K min}^{-1}$.

participating in a tunnel recombination.

Additional information on recombination luminescence of CaSO_4 phosphors has been obtained in the investigation of PSL. Figure 5 demonstrates the stimulation spectra of PSL (for 3.97 eV emission of Gd^{3+} ions) in $\text{CaSO}_4:\text{Gd}^{3+},\text{Na}^+$ and $\text{CaSO}_4:\text{Gd}^{3+},\text{F}^-$ phosphors irradiated by 10.5 eV photons at 80 K. The efficiency of PSL stimulation monotonously increases in a wide region starting from 2 eV and slows down at 3 eV. It is notable that the stimulation spectrum for 2.7 eV emission of Dy^{3+} centers in $\text{CaSO}_4:\text{Dy}^{3+}$ measured in a wider spectral range has a maximum at $\sim 3.65 \text{ eV}$ [20]. In alkali halides, a shape of stimulation spectrum for PSL associated with the release of electrons from F centers (an electron in a field of an anion vacancy) coincides with the absorption band of F centers (typical bandwidth of about 0.3 eV). In our opinion, the PSL registered in irradiated $\text{CaSO}_4:\text{Gd}^{3+}$ is caused by the photo-delocalization of holes, their migration to still localized electrons and

Figure 5. Stimulation spectra of PSL of 3.97 eV emission of Gd^{3+} ions in $\text{CaSO}_4:\text{Gd}^{3+}, \text{Na}^+$ (a), $\text{CaSO}_4:\text{Gd}^{3+}, \text{F}^-$ (b) and of Tb^{3+} blue emission in $\text{CaSO}_4:\text{Tb}^{3+}, \text{Na}^+$ (a - insert) phosphors irradiated by 10.5 eV photons at 80 K. The spectra are measured after irradiation (●●) or additional preheating of the irradiated phosphor to different temperatures. All spectra are measured at 80 K.

$e-h$ recombination providing the excitation of a neighbor Gd^{3+} and gadolinium line emission at the transition to the ground state (${}^6P_{7/2} \rightarrow {}^8S_{7/2}$).

According to Fig. 5, the intensity of PSL (for Gd^{3+} emission) at the stimulation by 2–3 eV photons in $\text{CaSO}_4:\text{Gd}^{3+}$ is practically invariant to temperature rise from 80 to 140 K, while PSL is completely absent at 225 K. The stimulation spectrum of PSL (for Tb^{3+} blue emission) in the irradiated $\text{CaSO}_4:\text{Tb}^{3+}, \text{Na}^+$ have been measured only at 2–2.5 eV. The PSL efficiency sharply decreases at the heating up to 140 K, and the PSL is totally annealed up to 260 K. In sodium containing phosphor there is an additional TSL peak at ~ 250 K. Under the same experimental conditions, we have not succeeded in detecting PSL in $\text{CaSO}_4:\text{Tb}^{3+}, \text{F}^-$. It should be stressed that in CaSO_4 phosphors irradiated by 8.4 eV photons causing the excitation of oxyanions, the intensities of phosphorescence, TSL and PSL are dozens of times lower than those in the phosphor irradiated by an equal dose of photons of $h\nu > E_g = 9.5$ eV.

The above-presented results confirm the suggestion that at the photocreation of separated e and h in CaSO_4 at 80 K, the holes undergo rapid localization at oxyanions, and the energy released at the recombination of mobile e with these localized h is sufficient for the excitation of single or pair terbium centers ($\text{Tb}^{3+}\text{Na}^+$ and $\text{Tb}^{3+}\text{Na}^+\text{Tb}^{3+}\text{Na}^+$) with the appearance of green and blue Tb^{3+} emission (${}^5D_4 \rightarrow {}^7F_1$ and ${}^5D_3 \rightarrow {}^7F_1$ transitions).

The localized holes of two types (O1 and O2 positions of oxygen ions) become mobile at a heating up to 110 and 155 K respectively, and recombine with the electrons still localized at some traps. According to theoretical calculations [21], there is a relatively small difference in energy of ground states for divalent and trivalent terbium or dysprosium ions, and all these levels are located within the energy gap ($E_g = 9.5$ eV) of CaSO_4 . Thermally released h can recombine with Tb^{2+} and Dy^{2+} with a typical emission of Tb^{3+} and Dy^{3+} centers. On the other hand, the calculated difference in energy for the ground state of Gd^{2+} and Gd^{3+} in an YPO_4 matrix is located below the top of a valence band [21]. By measuring the spectrum of subnanosecond intraband luminescence, the width of the valence band in CaSO_4 was estimated at about 7 eV [22], and it is unlikely that Gd^{3+} can trap e with the formation of Gd^{2+} . However, a compensator $[\text{F}^-|_0]^+$ with an effective positive charge located nearby Gd^{3+} can serve as a shallow electron trap. It is possible that in $\text{CaSO}_4:\text{Tb}^{3+}, \text{Cl}^-$ a similar electron trap is stable up to 250 K, when e gets released and recombines with h localized at V_{Ca} , causing the excitation of Tb^{3+} incorporated into a $[\text{V}_{\text{Ca}}\text{Tb}|\text{Ca}]^-$ center. The holes localized at such V_{Ca} -containing centers become mobile only with the sample heating up to ~ 400 K. Additional joint investigation of high-temperature TSL and the annealing of the EPR signal of trapped-hole centers (O^- nearby V_{Ca}) is needed to prove the proposed hypothesis.

4. Concluding remarks

A comparative investigation of the excitation spectra for impurity emission (Figs. 1 and 2), TSL (Figs. 3 and 4) and PSL (Fig. 5) has been performed for $\text{CaSO}_4:\text{Tb}^{3+}$ and $\text{CaSO}_4:\text{Gd}^{3+}$ phosphors co-doped with Na^+ (NaCl was added) or F^- (TbF_3 or GdF_3) ions. The analysis of the obtained results demonstrates that the TSL peaks at about 110 and 155 K correspond to the release of the holes localized near various defects and their recombination with localized electrons, causing the excitation of Tb^{3+} or Gd^{3+} emission. The annealing stages of PSL associated with photo-release of h correlate with the

main "hole" TSL peaks. The number of deep hole traps (TSL peaks at ~ 430 and ~ 560 K) connected with the presence of V_{Ca} increases at the co-doping of a phosphor with F^- ions (substitute for oxygen ions). The presence of Na^+ and Cl^- leads to the formation of shallow traps for e and h and to the tunnel recombination between the localized and spatially close e and h . TL that was earlier investigated in alkali halides [see, e.g., 9, 10] manifests as a distinguishing feature in $CaSO_4$ phosphors.

Traditionally, the tunneling gives birth to a luminescence centre in the lowest radiative state, while the higher excited states responsible for the quenching of luminescence above a certain temperature via nonradiative transitions are not involved in tunnel recombination. At the same time, at the recombination of a conduction electron with a localized h the luminescence centre firstly arises in a highly excited state. That is why the behavior of Tb^{3+} (and, probably, Gd^{3+}) emission is rather different in the region of ~ 220 and 440 K.

In conclusion, a special-purpose EPR study of the main hole and electron centers in $CaSO_4$ should be performed to support the suggested version of $e-h$ processes in the luminescence centers with complex structure.

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