Interplay of spin-allowed and spin-forbidden 5d–4f luminescence from rare earth ions

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Abstract

The conditions for co-existence of emissions from spin-allowed and spin-forbidden 5d–4f transitions in rare earth ions and for thermal quenching of these emissions have been analyzed by taking Tm^{3+} 5d–4f luminescence in $\text{LiYF}_4\text{:Tm}^{3+}$ and Lu^{3+} 5d–4f luminescence in LuF_3 as examples. It is shown that temperature behavior of 5d–4f luminescence agrees with the common trends in decreasing energy splitting between the lowest high-spin and low-spin 5d levels as well as decreasing energy gap between the lowest 5d level and the bottom of the conduction band of the host crystal towards heavier rare earth ions (from Er^{3+} to Lu^{3+}).

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It is well known, starting from the pioneering work of Yang and DeLuca [1], that some trivalent rare earth (RE) ions, in particular, Nd^{3+} , Er^{3+} , and Tm^{3+} , when doped into a wide bandgap host, emit luminescence in the vacuum ultraviolet (VUV) spectral range. This luminescence originates from $4f^{n-1}5d \rightarrow 4f^n$ interconfigurational transitions (the so-called 5d–4f luminescence) in the RE^{3+} ion. For the first half of the lanthanide series, transitions from the lowest $4f^{n-1}5d$ level into the $4f^n$ ground state are spin-allowed (SA) with short lifetimes (up to ≈ 50 ns). In the second half, such transitions are spin-forbidden (SF, lifetimes in the μs range) because the spin of the lowest $4f^{n-1}5d$ state, the so-called high-spin (HS) state, exceeds the spin of states in the ground $4f^n$ configuration. However, depending on the ion, the host, and the sample temperature, SA emission from the higher-lying low-spin (LS) $4f^{n-1}5d$ state can coexist with the SF emission [2,3].

Till recently, RE^{3+} luminescence in VUV has been detected only from Nd^{3+} , Er^{3+} , and Tm^{3+} . However, our studies [4,5] have shown that 5d–4f luminescence in VUV

($h\nu \sim 10$ eV) is also observed from Gd^{3+} and Lu^{3+} ions doped into some fluoride hosts with sufficiently wide energy gaps, e.g. into LiYF_4 . Gd^{3+} ions emit only fast SA 5d–4f luminescence as it is typical for RE^{3+} ions from the first half of the lanthanide series. At low temperatures, Lu^{3+} ions emit slow SF 5d–4f luminescence exclusively. However, with the increase in temperature up to ~ 100 K, an admixture of SA 5d–4f emission appears [5]. A similar temperature dependence was observed for Er^{3+} SA and SF 5d–4f luminescence from $\text{LiYF}_4\text{:Er}^{3+}$ crystals, but at much higher temperatures above 800 K [6]. To the best of our knowledge no data on the behavior of Tm^{3+} SA and SF 5d–4f luminescence at high temperatures have been reported.

In the present work, temperature dependences of VUV luminescence due to interconfigurational 5d–4f transitions of Tm^{3+} doped into LiYF_4 as well as of Lu^{3+} in LuF_3 have been investigated experimentally and respective models describing the observed phenomena were developed.

The measurements were performed at the SUPERLUMI station [7] of HASYLAB at DESY, using synchrotron radiation from the DORIS storage ring for excitation. The time-resolved spectra of VUV luminescence were recorded with a Pouey-type monochromator (typical spectral

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resolution $\Delta\lambda = 20 \text{ \AA}$) equipped with a CsI-sensitized microsphere-plate detector. Discrimination between the fast and slow emissions was achieved by measuring signals within the “short” and “long” time windows (Δt), the latter delayed (by δt) with respect to excitation pulse of synchrotron radiation. Single crystals of LiYF_4 doped with 1.0 at% Tm^{3+} were grown by the Czochralski method. The powder sample of LuF_3 was a high-purity chemical.

Emission spectrum due to 5d–4f transitions of Tm^{3+} in LiYF_4 was investigated in a wide temperature range up to $\sim 790 \text{ K}$ (Fig. 1) when this emission is practically quenched thermally (Fig. 2). At sufficiently low temperatures, the fast ($\tau = 5 \text{ ns}$ at 300 K [8]) and slow emissions due to SA and SF 5d–4f radiative transitions co-exist, but at higher tempera-

Fig. 2. Temperature dependence of integrated intensity of VUV luminescence from LuF_3 , $\text{LiYF}_4:\text{Tm}^{3+}$, and $\text{LiYF}_4:\text{Er}^{3+}$. The curves are best fits of experimental points with the Mott formula $I(T)/I(0) = (1 + A \exp(-\varepsilon_a/k_B T))^{-1}$ (activation energy ε_a and pre-exponent factor A are fitting parameters, k_B is the Boltzmann constant).

Fig. 1. Normalized time-resolved spectra of VUV emission due to Tm^{3+} 5d–4f transitions in $\text{LiYF}_4:\text{Tm}^{3+}$ measured at different temperatures with “short” ($\Delta t = 13.5 \text{ ns}$, $\delta t = 0$) and “long” ($\Delta t = 127 \text{ ns}$, $\delta t = 50 \text{ ns}$) time windows. The terminal Tm^{3+} 4f multiplets are marked for SA and SF transitions. The decomposition of the spectra into the sum of Gaussians is also shown.

tures the fast emission bands disappear. This is caused by an increase in the probability for nonradiative relaxation from the higher-lying LS 5d state to the lower-lying HS 5d state, and at temperatures high enough the rate of nonradiative decay exceeds that of the radiative decay. With a further increase in temperature, when a thermal equilibrium between HS and LS states is reached, SA luminescence reappears, but with slow decay times. The “indirect” thermal mechanism populates the LS 5d state and therefore, the decay kinetics for SA emission is determined by the slow lifetime of SF transitions. As expected, the emission bands also possess a considerable temperature broadening.

The temperature dependence of 5d–4f luminescence from Er^{3+} doped into LiYF_4 was also investigated in the temperature range up to 790 K (Fig. 2). However, technical reasons prohibited reaching temperatures above 800 K , where Er^{3+} SA 5d–4f luminescence reappears, according to Ref. [6]. Nevertheless, it was clearly shown that thermal quenching of 5d–4f luminescence occurs for Er^{3+} at temperatures higher than that for Tm^{3+} .

Similar to results obtained in Ref. [5] for LiLuF_4 and $\text{LiYF}_4:\text{Lu}^{3+}$, only SF 5d–4f luminescence of Lu^{3+} is observed from LuF_3 at low temperatures (see Fig. 3). However, an increase in temperature above 100 K causes the appearance of an additional higher-energy emission band due to SA 5d–4f transitions. Analogously to the case of Er^{3+} or Tm^{3+} ions, a temperature increase opens another decay channel for the lowest HS ($S = 1$) $4f^{13}5d$ level of Lu^{3+} , namely the thermal population of the higher-lying LS ($S = 0$) $4f^{13}5d$ state, from which the 5d–4f radiative transition is spin-allowed.

The energy separations between the SA and SF 4f–5d transitions in Er^{3+} and Tm^{3+} doped into LiYF_4 are 3330

Fig. 3. Normalized spectra of VUV emission due to Lu^{3+} 5d–4f transitions in LuF_3 measured at different temperatures.

and 2070 cm^{-1} , respectively [9]. Taking into account the trend of decreasing energy splitting between SA and SF 4f–5d transitions from Tb^{3+} to Yb^{3+} , and that this splitting is of the order of 1500 cm^{-1} in Yb^{3+} [9], one can expect an even lower value for this splitting in Lu^{3+} . Indeed, the value given in Ref. [5] for this splitting in $\text{LiYF}_4:\text{Lu}^{3+}$ is 823 cm^{-1} , i.e. of the order of two phonon energies. As a result, the rate of phonon relaxation exceeds the radiative decay of the higher-lying LS 5d state of Lu^{3+} , and accordingly at low temperature only SF 5d–4f luminescence from Lu^{3+} is observed. Due to the same trend, SA 5d–4f luminescence from Lu^{3+} appears at much lower temperature (after thermal equilibrium between HS and LS 5d levels in Lu^{3+} is reached) compared with Tm^{3+} .

For Tm^{3+} the highest-energy excited 4f level ($^3\text{P}_2$) is situated at $\sim 38,200\text{ cm}^{-1}$ (we do not consider $^1\text{S}_0$ level which has very high energy $\sim 75,000\text{ cm}^{-1}$), the energy of the lowest HS 5d level is $\sim 61,000\text{ cm}^{-1}$ [9], i.e. the energy gap

between the $^3\text{P}_2$ state and the lowest 5d levels is $\sim 22,800\text{ cm}^{-1}$. This energy gap exceeds more than 40 times the cut-off phonon energy in this crystal host, making the mechanisms of thermal quenching for Tm^{3+} 5d–4f luminescence due to nonradiative relaxation to 4f levels improbable. Therefore, only thermally activated ionization of 5d electrons into the conduction band is responsible for thermal quenching in the case of the Tm^{3+} ion. The Er^{3+} ion has some 4f levels ($^2\text{F}(2)_{5/2}$ and $^2\text{F}(2)_{7/2}$) with energies close to the emitting 5d levels, and relaxation via 4f levels can contribute to the quenching of Er^{3+} 5d–4f luminescence.

The Lu^{3+} ion has no excited 4f levels and therefore, thermal quenching of Lu^{3+} 5d–4f luminescence is attributed to thermally activated ionization of 5d electrons to the conduction band. By taking into account the trend of decreasing energy separation between the lowest 5d level and the bottom of the conduction band towards heavier REs [10], one can expect that 5d–4f luminescence will be quenched at lower temperatures for heavier REs. Indeed, thermal quenching of Er^{3+} 5d–4f emission (in LiYF_4) occurs at $T > 500\text{ K}$, whereas thermal quenching of Tm^{3+} 5d–4f emission (in LiYF_4) already starts at $\sim 450\text{ K}$ (see Fig. 2). Data on Yb^{3+} 5d–4f emission are not available since this emission has never been detected. Anyway, thermal quenching of Lu^{3+} 5d–4f emission is supposed to occur at a much lower temperature than that of Er^{3+} and Tm^{3+} 5d–4f emission, since, according to Ref. [10], the lowest 5d level of Lu^{3+} is situated closer to the conduction band by $\sim 2100\text{ cm}^{-1}$ than to the lowest 5d level of Er^{3+} . Indeed, our experiments show that Lu^{3+} 5d–4f luminescence is already thermally quenched at temperatures $T > 100\text{ K}$ (Fig. 2).

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