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Conversion of VUV to visible light and the structure of the 5d levels in $K_5Li_2LaF_{10}$:Tb

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Abstract

Upon UV–VUV excitation terbium doped $K_5Li_2LaF_{10}$ emits white light coming from the $^5D_3$ and $^5D_4$ multiplets for content of Tb^{3+} up to 10 at%. For higher concentrations (80 and 100 at%) the emission becomes green. In excitation spectrum, recorded at 12 K, the positions of the zero-phonon lines are not well determined. The spin allowed f–d transitions in this spectrum are similar to the cerium one in $K_5Li_2LaF_{10}$: Ce^{3+}, as van Pieterson proposed in the frames of Dorenbos' model. The maxima of these terbium f–d transitions are found at: 46,976, 57,124, 59,404, 60,629 and 67,110 cm^{-1}. The lowest forbidden, high-spin d band is situated at 39,193 cm^{-1}. The lifetime of the $^5D_4$ multiplet is 7.5 ms and does not depend on the terbium concentration, but the $^5D_3$ lifetimes are strongly influenced and amount to: 2710, 2130, 14.1, 9.5 μs for 2, 10, 80, 100 at% of terbium, respectively. This is in agreement with the colour rendering of these samples.

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Keywords: Luminescence; Fluoride crystal; VUV; Lanthanide

1. Introduction

Lanthanide doped phosphors have been investigated for more than 100 years. In the past, the interest was focused mainly on oxide materials. Nowadays the demand is growing in the search of good candidates in wide band gap crystal group, especially fluorides, because of the need to find good phosphors for mercury free lamps and plasma display panels. For fluoride host crystals, the fundamental absorption edge is located in VUV region – typically at above 80,000 cm^{-1} (125 nm) [1]. It gives the possibility for investigation not only, the well theoretically predicted, $4f^n$–$4f^n$ transitions [2,3] but also $4f^{n-1}$–5d one. The parity forbidden intraconfigurational $4f^n$ transitions are shielded against the influence of neighbour ion interaction by full $5s^2$ and $5p^6$ shells. The $4f^{n-1}$–5d transitions are parity allowed, with higher influence of environment to them which results in intense absorption bands and widely vibronic character due to the large radial extension of 5d orbitals.

Some generalisations in the $4f^{n-1}$–5d transitions were done in the past. Dorenbos compared several $4f^{n-1}$–5d transitions for all lanthanide ions in different matrices and came to the conclusion that if the energy of spin-allowed transition of certain lanthanide ion is known for a specific compound, the transition energy of other lanthanides can be predicted for the same compound [4,5]. Van Pieterson found that there should be the similarity between the Ce^{3+} and Tb^{3+} $4f^{n-1}$–5d transition structure. However, the interaction of more 4f electrons with 5d electron gives more complicated spectrum. For heavy lanthanide (Tb–Lu), besides low-spin (LS), spin-allowed f–d transitions, the high-spin (HS) can be seen at lower energy.

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The LS–HS splitting is mainly caused due to Coulomb interaction between the 4f electrons and 5d electron [6,7].

2. Experimental

Single $K_5Li_2LaF_{10}$:Tb crystals were grown by vertical Bridgman method in graphite crucibles made from high quality IG-110 purified graphite. The crystal is orthorhombic (space group $D_{2h}^{16} - Pnma$). Its structure is built from layers perpendicular to the *a*-axis, formed by LnF_8 dodecahedra and LiF_4tetrahedra. Lanthanide and lithium ions occupy sites with point C_s symmetry whereas potassium and fluorine ions occupy sites with C_s and C_1 symmetry. The LnF_8 polyhedra do not share fluorine ions and the closest lanthanide ions are separated more than 6.5 Å. Owing to these features, exchange interactions between Ln ions may be neglected. Based on crystallographic structure, there is only one site for the lanthanide ions.

Excitation spectra, and the VUV excited luminescence spectra were recorded using synchrotron radiation at the SUPERLUMI station of the Synchrotronstrahlungslabor at DESY in Hamburg. In luminescence decay time measurements, short (4 ns) pulses delivered by the optical parametric oscillator OPO (Continuum, Surelite I) pumped by the third harmonic of Nd:YAG laser were used to excite directly luminescence levels. Luminescence was dispersed by 1 m double-grating monochromator GDM-1000, detected by the Hamamatsu R-928 PMT. The decay signal was averaged and stored with the Tektronix TDS 3052 digital oscilloscope. For low temperature measurements a continuous flow helium cryostat (Oxford model CF 1204), equipped with a temperature controller was used.

3. Results and discussion

Fig. 1 presents the low temperature (12 K) excitation spectrum of the $K_5Li_2La_{0.98}Tb_{0.02}F_{10}$ crystal. It is composed of HS, A, B, C, D, E, F, G, H, I, J, K and L peaks located at: 39,193, 46,853, 48,080, 49,805, 51,763, 55,167, 57,125, 58,487, 59,404, 60,629, 67,111, 74,737 and 79,658 cm^{-1}, respectively. The HS and A are associated with high-spin and the lowest low-spin $4f^{n-1}$–5d transitions, with energy distance HS–LS 7660 cm^{-1}. This value is in perfect agreement with 7700 ± 750 cm^{-1} evaluated for numerous terbium-doped matrices [5]. However, it should be noticed that other values were also reported in literature: 7010 ± 860, 6300 ± 900 and 4870 ± 750 cm^{-1} [4,5]. Association of others peaks is more problematic. Therefore the excitation spectrum of $K_5Li_2La_{0.87}Ce_{0.13}F_{10}$ was considered, which should be similar to the terbium-containing sample and less complicated [7]. The cerium spectrum was shifted 13,200 cm^{-1}, which is in the frames of Dorenbos' calculations [5]. Consequently, the peaks F, H, I, J can be associated with LS $4f^{n-1}$–5d transitions, whereas B, C, D and G seems to be the HS transitions in nature. The last two peaks K and L might be ascribed to the exciton and fundamental absorption band. The origin of the E band seems to be a defect one in a heavily (13 at%) cerium doped crystal.

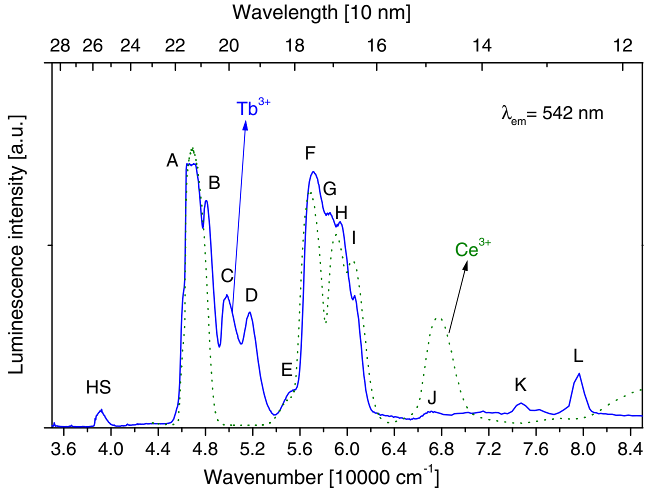

Fig. 1. Excitation spectrum $K_5Li_2La_{0.98}$ $Tb_{0.02}F_{10}$ at 12 K. Emission was monitored at 542 nm (solid line) with the comparison of Ce^{3+} d levels structure in $K_5Li_2LaF_{10}$ (doted line). The cerium spectrum was shifted 13,200 cm^{-1} due to Dorenbos calculations.

The concentration-depended luminescence spectra of doped with 2 and 100 at% of terbium crystals are shown in Fig. 2. Upon UV–VUV excitation terbium doped $K_5Li_2LaF_{10}$ crystal emits white light coming from the $^5D_3$ and $^5D_4$ multiplets for content of Tb^{3+} up to 10 at%. For higher terbium concentration, the emission becomes green, due to self-quenching of the $^5D_3$ luminescence. Both, presented in the Fig. 2 spectra are identical in the red–blue part. In this region, the emission was ascribed to be arising from the $^5D_4$ multiplet. The maximum of its luminescence was observed for the $^5D_4 \rightarrow {}^7F_5$ transition with two maxima at 18,280 and 18,432 cm^{-1} (547.05, 542.53 nm). Above 20,710 cm^{-1} these two spectra are completely different. In

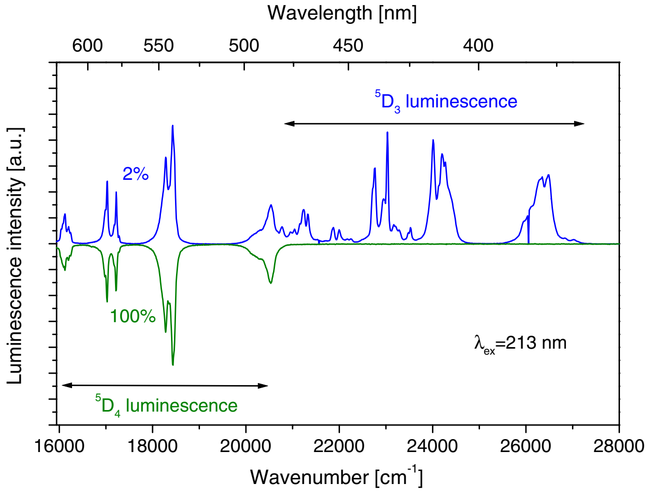

Fig. 2. Room temperature luminescence spectra of $K_5Li_2La_{0.98}$ $Tb_{0.02}F_{10}$ and $K_5Li_2TbF_{10}$ crystals upon excitation at 213 nm. For better visualisation of this picture, the $K_5Li_2TbF_{10}$ luminescence is shown inverted.

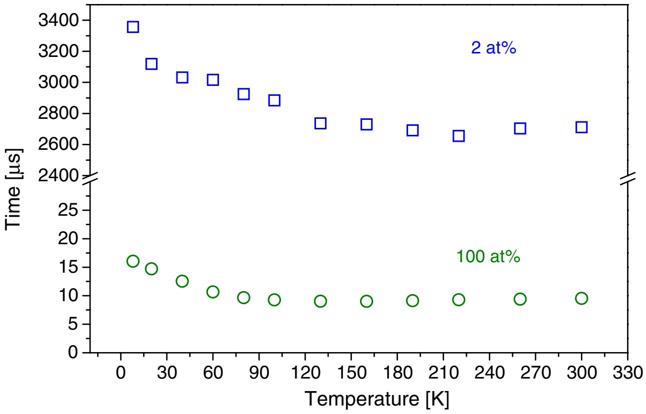

Fig. 3. Temperature dependence of the $^5D_3$ state lifetime in $K_5Li_2La_{0.98}$-$Tb_{0.02}F_{10}$ and $K_5Li_2TbF_{10}$ crystals.

the $K_5Li_2La_{0.98}Tb_{0.02}F_{10}$ the strong emission from the $^5D_3$ to all ^7F_J states is present. The nonradiative quenching of the $^5D_3$ luminescence is caused by the resonance cross-relaxation between excited states and the ground states of two Tb^{3+} and can be described as [8]:

$$Tb^{3+}(^5D_3) + Tb^{3+}(^7F_6) = Tb^{3+}(^5D_4) + Tb^{3+}(^7F_0) \qquad (1)$$

The lifetime of the $^5D_4$ multiplet is ~7.5 ms and does not depend on the terbium concentration or temperature. On the contrary, the $^5D_3$ lifetimes are strongly influenced and amount to: 2710, 2130, 14.1, 9.5 µs for 2, 10, 80, 100 at% of terbium, respectively. Fig. 3 presents lifetimes of the $^5D_3$ state of Tb^{3+} in $K_5Li_2La_{0.98}Tb_{0.02}F_{10}$ and $K_5Li_2TbF_{10}$ crystals. At 8 K the lifetime of the $^5D_3$ multiplet in $K_5Li_2La_{0.98}Tb_{0.02}F_{10}$ reaches 3356 µs and decreases to 2710 µs at room temperature. In $K_5Li_2TbF_{10}$ the analysed lifetimes are 16 and 9.5 µs for 8 and 300 K, respectively.

4. Conclusions

The $K_5Li_2LaF_{10}$ crystals doped with Tb^{3+} were found to be good phosphors. For heavy doped with Tb^{3+} samples the luminescence is green due to concentration quenching of $^5D_3$ luminescence. The detailed information about the structure of the 5d levels of Tb^{3+} was presented and it is with an agreement with theoretical predictions of van Pieterson and Dorenbos.

Acknowledgements

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