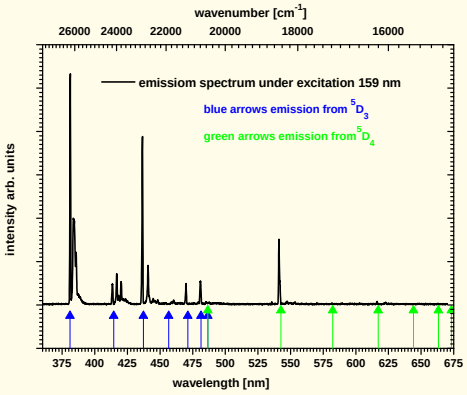
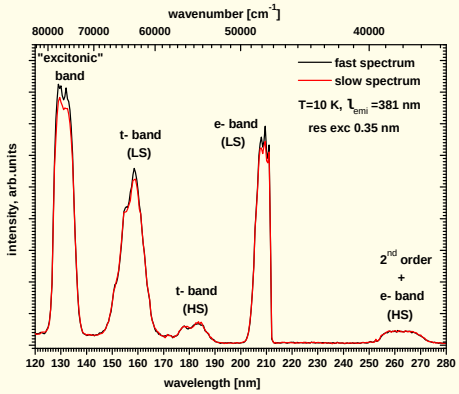
HIGH AND LOW SPIN ENERGY STATES OF THE Tb^{3+} $4f^7 5d$ CONFIGURATION IN BaF_2

Marcin Witkowski and Andrzej J. Wojtowicz
Uniwersytet Mikołaja Kopernika, Instytut Fizyki ul. Grudziądzka 5/7, Toruń, Polska

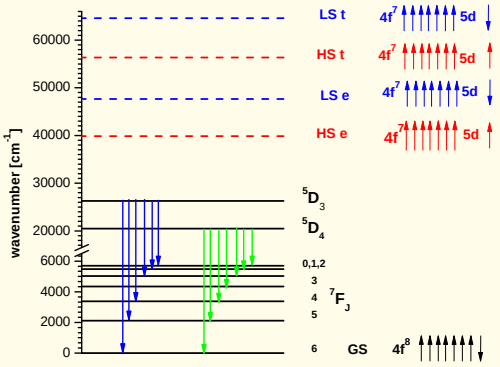
Excitation and emission spectra



Emission spectrum under excitation at 159 nm (d - band)
(Res. exc. 0.35 nm, res. emi. 2.7 nm, T 10 K, step 0.5 nm)

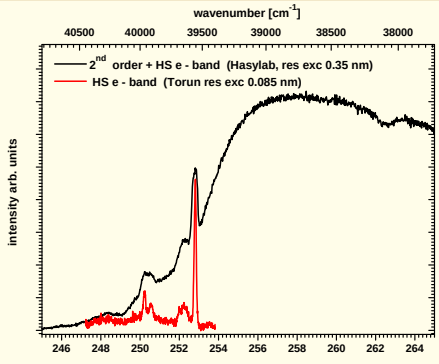


Time resolved excitation spectra dominant blue Tb emission line at 381 nm
(Res. exc. 0.35 nm, res. emi. 2.7 nm, T 10 K, step 2 nm)



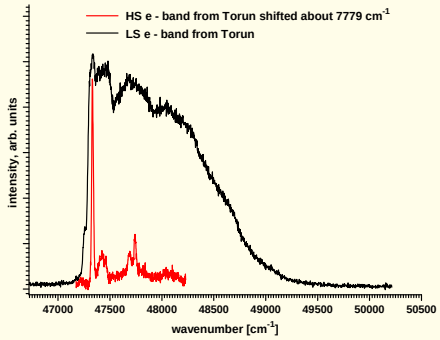
Energy level diagram of Tb^{3+} ion

Excitation spectra of Tb^{3+} blue emission measured at Hamburg and Toruń



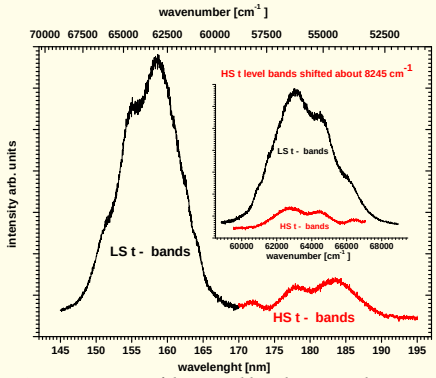
(Hamburg: res. exc. 0.35 nm, res. emi. 10.8 nm, T 10 K, step 0.02 nm)
(Toruń: res. exc. 0.085 nm, res. emi. 7.5 nm, T 10 K, step 0.025 nm)

High spin and low spin e - bands, comparison



Excitation spectra of dominant blue Tb emission line at 381 nm
(res. exc. 0.085 nm, res. emi. 7.5 nm, T 10 K, step 0.025 nm)

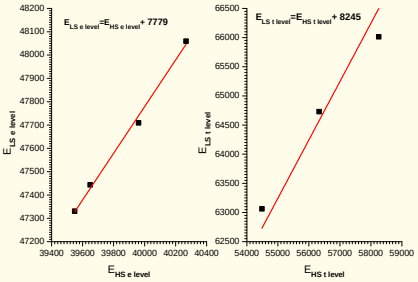
High spin and low spin t - bands



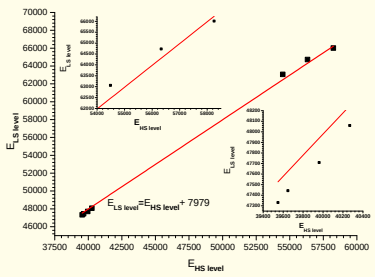
Excitation spectra of dominant blue Tb emission line at 381 nm
(res. exc. 0.14 nm, res. emi. 21.6 nm, T 10 K, step 0.01 nm)
Inset: Comparison HS and LS t - level bands

Wide energy gap materials activated with rare earth ions play an important role in optoelectronics (phosphors, lasers and scintillators). A widely studied example is provided by a Tb^{3+} ion, well known and widely applied because of its bright blue and green luminescence. Interestingly some details (weak bands) in the excitation spectra of Tb^{3+} emissions have only recently been studied in detail and understood [1, 2]. In these papers the authors identify some weak bands at low energy side of the dominant and well known f-d bands as being due to spin-forbidden transitions from the $^7F_6$ ($4f^8$) ground state to the high spin (HS) states of the Tb^{3+} $4f^7 5d$ configuration. The dominant bands are interpreted, consequently, as being due to the spin-allowed transitions originating in the ground state and terminating at the low spin (LS) levels of the $4f^7 5d$ configuration of Tb^{3+} ion. The energy difference between the lowest energy HS and LS states (exchange energy) is due to the Coulomb interaction between 4f and 5d electrons and has been measured to assume, for Tb^{3+} in $LiYF_4$, a respectable value of nearly $8000\,cm^{-1}$ [2].

In this Communication we report results of detailed spectroscopic studies of Tb^{3+} luminescence from BaF_2 : 0.075% Tb performed at home (IF UMK Torun) and at Superlumi station in Hasylab (DESY, Hamburg, Germany). We have measured UV/VUV excitation spectra of the dominant blue Tb^{3+} luminescence, and emission spectra under excitation into various bands found from the excitation spectra. The excitation spectra are dominated by the well known broad LS bands due to the crystal field induced 10Dq splitting of the d-electron energy. The higher energy triple t-band and unresolved single e-band at lower energy are widely separated (about $15000\,cm^{-1}$)[3].



LS peaks vs. HS peaks

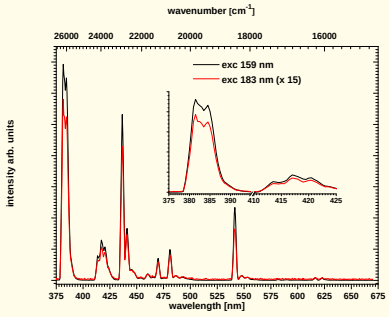


LS peaks vs. HS peaks

In addition to these bands we have also detected a number of weaker bands at lower energy sides of both dominant LS bands. While the bands at 252.8, 252.3, 250.4 and 248.4 nm clearly correspond to HS bands found earlier by Meijerink and coworkers in $LiYF_4$: Tb [1, 2] the bands at 183, 178 and 172 nm have been never, to the best of our knowledge, reported before. We present arguments that these bands are the HS counterparts of the triple LS t-band at about 158 nm. The $5d(e) - 4f$ (E_{1ex}) and $5d(t) - 4f$ (E_{2ex}) exchange energies are nearly the same (about $8000\,cm^{-1}$).

$$E_{1ex} = \left\langle 4f5d_e \left| \frac{1}{r} \right| 5d_e 4f \right\rangle \quad \neq \quad E_{2ex} = \left\langle 4f5d_t \left| \frac{1}{r} \right| 5d_t 4f \right\rangle$$

Selectively excited emission spectra



Emission spectra upon excitation 159 and 183 nm
(Res. exc. 0.35 nm, res. emi. 2.7 nm, T 10 K, step 0.5 nm)

Acknowledgments

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References

[1] R.T. Wegh, A. Meijerink, Phys. Rev. B **60** (1999) 10820.
[2] L. van Pieterson, R.T. Wegh, and A. Meijerink, J. Chem. Phys. **115** (2001) 9382.
[3] W.J. Manthey, Phys. Rev. B **8** (1973) 4086.