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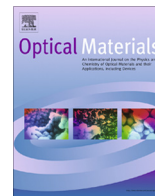
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## VUV spectroscopy of complex fluoride systems $\text{Na}_{0.4}(\text{Y}_{1-x}\text{RE}_x)_{0.6}\text{F}_{2.2}$ ( $\text{RE}^{3+} = \text{Nd}^{3+}, \text{Tm}^{3+}$ )

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$\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}:\text{Tm}^{3+}$

## ABSTRACT

Emission and excitation spectra as well as luminescence decay kinetics of complex non-stoichiometric fluoride crystals  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Nd}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.005, 0.05, 0.2, 1$ ) and  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Tm}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.0005, 0.01, 0.05, 0.1$ ) have been studied in the VUV spectral range at liquid-helium ( $T \sim 10$  K) temperatures. It has been shown that these crystals show intense broad-band VUV luminescence due to the interconfiguration 5d–4f transitions in  $\text{Nd}^{3+}$  and  $\text{Tm}^{3+}$  ions. Remarkable concentration quenching is observed for  $\text{Nd}^{3+}$  5d–4f luminescence whereas fast (spin-allowed) 5d–4f luminescence of  $\text{Tm}^{3+}$  shows no concentration quenching for the studied doping level up to 10%. The spin-allowed 5d–4f luminescence of  $\text{Tm}^{3+}$  in these crystals was found to be rather weak compared to spin-forbidden 5d–4f luminescence because of efficient nonradiative relaxation from higher-energy 5d states of  $\text{Tm}^{3+}$  to the lowest-energy 5d level responsible for spin-forbidden 5d–4f luminescence. The studied fluoride systems can be considered as promising active media for the development of VUV solid state lasers with optical pumping.

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### 1. Introduction

During previous years many new crystalline systems optically active in the vacuum ultraviolet (VUV) spectral range were produced and studied, mainly because of the strong interest in VUV excited phosphors for mercury-free fluorescent lamps and plasma displays as well as to possible active media for solid-state VUV lasers. Most of those VUV systems are based on 5d–4f luminescence of some trivalent rare earth ( $\text{RE}^{3+}$ ) ions emitting in VUV spectral region, namely, of  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ , and  $\text{Tm}^{3+}$  [1–4], doped into wide band-gap (mostly fluoride) hosts. This 5d–4f luminescence of  $\text{RE}^{3+}$  ions is caused by transitions from the lowest level of the  $4f^{n-1}5d$  electronic configuration (hereafter – the lowest 5d level) to the ground state or some excited levels of the  $4f^n$  electronic configuration (4f levels) of the  $\text{RE}^{3+}$  ion. For the first half of the lanthanide series, transitions from the lowest 5d level to the 4f levels are spin-allowed (SA) and 5d–4f luminescence is fast with typical lifetimes in the nanosecond range. In the second half of the series, transitions from the lowest 5d state (so-called high-spin (HS) state, with value of spin higher than that in the ground state) are spin-forbidden (SF) [2], and such SF 5d–4f luminescence is slow with lifetimes in the  $\mu\text{s}$  range. However, depending on the particular

ion, the host, and the temperature, SA 5d–4f luminescence from the higher-energy, so-called low-spin (LS) 5d state, with the same value of spin as in the ground state, can coexist with SF 5d–4f luminescence.

Non-stoichiometric fluoride compounds  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{RE}_x)_{0.6}\text{F}_{2.2}$  well suit the requirements set for optical crystalline materials in the VUV range. The host crystal  $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$  has high transparency in VUV [5,6], high hardness, is non-hydroscopic, and large single crystals can be grown from the melt using standard techniques, in particular the Bridgman method [5]. The system  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{RE}_x)_{0.6}\text{F}_{2.2}$  has high capacity for doping  $\text{RE}^{3+}$  ions, up to the complete substitution of  $\text{Y}^{3+}$  for most  $\text{RE}^{3+}$  ions.  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{RE}_x)_{0.6}\text{F}_{2.2}$  crystals have a disordered cubic fluorite structure of space group  $\text{Fm}\bar{3}\text{m}$ , where cations are statistically distributed through (0 0 0) and face-centered positions in the unit cell. The compensation of the difference in cation charges takes place in the anion sublattice, where fluorine ions can occupy three different sites [7]. The site symmetry of cation positions is approximately  $\text{C}_{4v}$  [8].

VUV luminescence properties of this type of fluoride systems doped with  $\text{Er}^{3+}$ :  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Er}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0, 0.01, 0.1, 1$ ) have been studied in [9]. Both fast SA and slow SF 5d–4f luminescence of  $\text{Er}^{3+}$  have been detected. In the present work the time-resolved spectroscopic studies in the VUV spectral range of fluoride systems  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Nd}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.005, 0.05, 0.2, 1$ ) and  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Tm}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.0005, 0.01, 0.05, 0.1$ ) have been performed, data on the ener-

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gies of the lowest  $5d$  levels of  $\text{RE}^{3+}$  ions in the host material  $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$  have been analyzed and possibilities of using these systems as VUV laser media are considered.

## 2. Experiment

The measurements of emission and excitation spectra as well as of luminescence decay curves were performed at the SUPERLUMI station [10] of HASYLAB at DESY under the excitation by synchrotron radiation (60–190 nm) from the DORIS storage ring. The excitation spectra were recorded with an instrumental resolution of the primary monochromator of 0.3 nm. The measurements of UV/VUV emission spectra and the spectral selection of the bands for decay curves measurements were carried out using a 0.5 m Pouey-type secondary monochromator equipped with a solar-blind (Hamamatsu R6836) photomultiplier tube for spectral measurements and with a microsphere plate detector for measurements of decay curves. It should be pointed out that the recorded emission spectra are resolution limited, as the UV/VUV secondary monochromator is not designed for high resolution spectroscopy: the typical spectral bandpass was  $\Delta\lambda = 2$  nm. The time correlated single-photon counting was used for time-resolved spectra and decay curve measurements. The time resolution of the detection system was about 0.1 ns with a 130 ps length of the exciting synchrotron radiation pulses followed with the period of 192 ns. The width of the time gate for the measurement of time-resolved spectra was varied between 10 and 150 ns depending on the decay time of the component measured. The delay of the gate with respect to the peak of excitation pulses was 0.5 or 50 ns for the measurements of the fast or slow component respectively. A 0.3-m Czerny-Turner monochromator-spectrograph SpectraPro-308i (Acton Research Inc.) with a R6358P (Hamamatsu) photomultiplier tube was applied for selecting the monitored wavelength when measuring excitation spectra of emissions in UV/visible spectral range. Emission spectra in the spectral range 200–700 nm were recorded at the same spectrograph with a liquid nitrogen cooled CCD detector (Princeton Instruments Inc.). Spectral resolution was  $\sim 0.2$  nm with a 1200 grooves/mm grating. Emission spectra were not corrected for the spectral response of the detection system.

$\text{Na}_{0.4}(\text{Y}_{1-x}\text{Nd}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.005, 0.05, 0.2, 1$ ) and  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Tm}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.0005, 0.01, 0.05, 0.1$ ) crystals were grown by Bridgman method in the carbon heating site in the fluorine atmosphere created by the thermal decomposition of Teflon [5]. Multicellular carbon crucibles were used for the growth procedure. The growth rate was 3–5 mm/h. Polished platelets of 1 mm thickness and 1 cm diameter were used for the measurements. The samples were mounted onto a copper sample holder attached to a cold finger of a flow-type liquid helium cryostat.

## 3. Results and discussion

Emission spectra of  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Nd}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.005, 0.05, 0.2, 1$ ) measured at a temperature of 14 K under  $4f^3\text{--}4f^25d$  excitation at 176/179 nm are presented in Fig. 1. The broad emission bands are due to parity- and spin-allowed interconfiguration  $4f^25d\text{--}4f^3$  transitions in  $\text{Nd}^{3+}$  with the shortest-wavelength band (peaked at 182.5 nm for  $x = 0.005$ ) corresponding to transitions from the lowest  $5d$  level to the ground state multiplet term  $^4I_{9/2,11/2,13/2,15/2}$  of  $\text{Nd}^{3+}$  ions. The maximum intensity of  $\text{Nd}^{3+}$   $5d\text{--}4f$  luminescence is observed for the  $x = 0.005$  sample whereas for the  $x = 1$  sample the luminescence intensity is very weak, i.e. considerable concentration quenching is observed for  $\text{Nd}^{3+}$   $5d\text{--}4f$  luminescence. In contrast to many other hosts (see e.g. [3,4]), the narrow lines arising from parity-forbidden intraconfiguration  $4f^3\text{--}4f^3$  transitions from

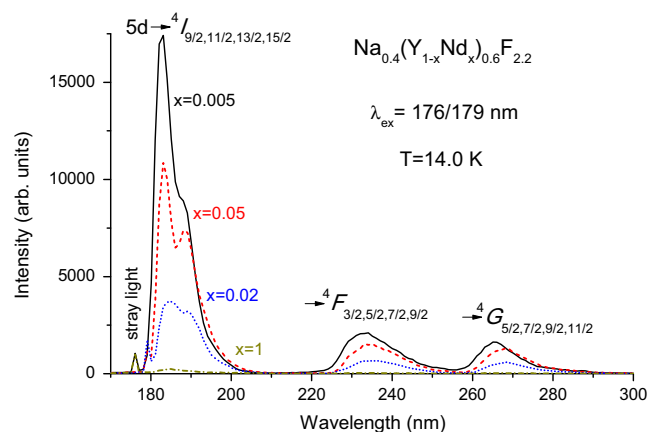


Fig. 1. Emission spectra of  $\text{Nd}^{3+}$   $5d\text{--}4f$  luminescence in  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Nd}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.005, 0.05, 0.2, 1$ ). The assignments of the bands to particular transitions are shown. Excitation wavelength was between 176 and 179 nm.

the  $^2G(2)_{9/2}$  level of the  $\text{Nd}^{3+}$  ion are not observed. This means that at least at low temperature there is no efficient nonradiative relaxation from  $5d$  to  $4f$  levels of  $\text{Nd}^{3+}$  in this host.

The threshold in the excitation spectra of  $\text{Nd}^{3+}$   $5d\text{--}4f$  luminescence at about 183 nm (Fig. 2) corresponds to the onset of  $\text{Nd}^{3+}$   $4f^3\text{--}4f^25d$  absorption. Luminescence intensity drops to zero for the region  $\lambda < 120$  nm. From the measurements of reflection spectra of the studied samples (not shown) the estimations of energy bands parameters of the host crystal have been made: the peak energy of the exciton band is  $\sim 10.95$  eV ( $\lambda \sim 113$  nm) and the band gap is  $\sim 11.35$  eV. Therefore the spectral range  $\lambda < 120$  nm corresponds to the region of the host absorption and so there is no energy transfer from the host, including exciton region, to  $5d$  levels of  $\text{Nd}^{3+}$ .

The single-exponential decay with decay time of 16.5 ns was obtained at low temperature for  $5d\text{--}4f$  luminescence of  $\text{Nd}^{3+}$  only for small doping concentration (Fig. 3). For higher concentrations of  $\text{Nd}^{3+}$ , shortening and non-exponentiality of decay is observed due to luminescence quenching. The initial stage of faster decay and the decrease of decay time at the extended stage of decay are the characteristic features of concentration quenching [11]. This effect occurs due to the nonradiative direct (resonance) or non-direct (cross-relaxation) energy transfer from the  $5d$  level of

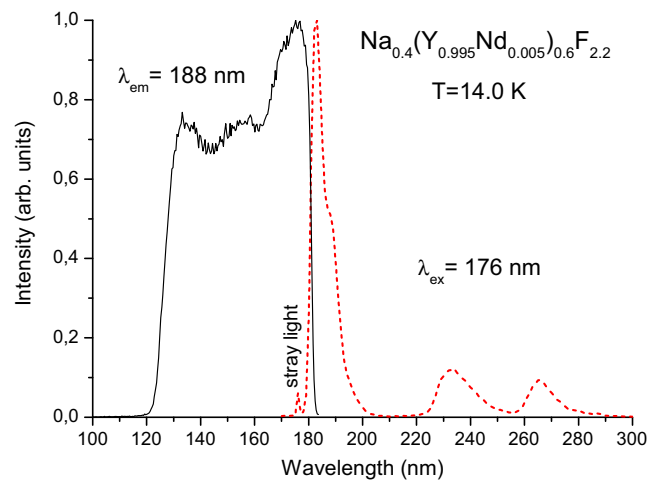
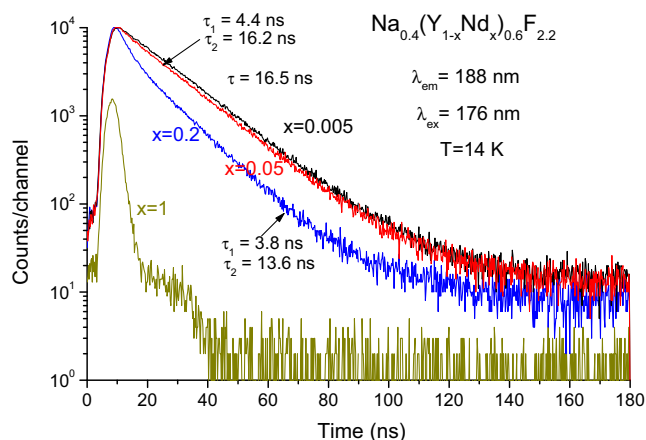


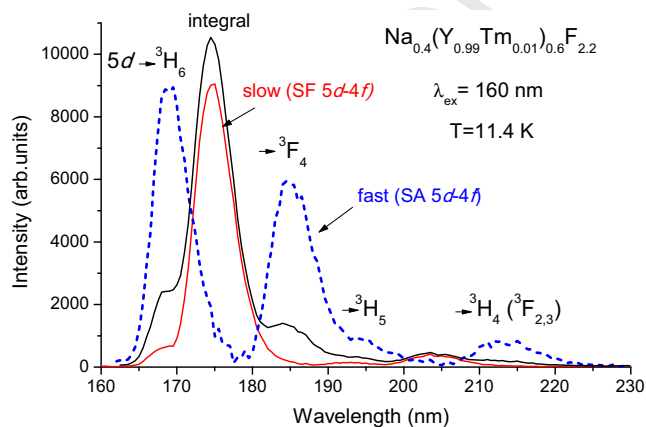
Fig. 2. Excitation spectrum of  $\text{Nd}^{3+}$   $5d\text{--}4f$  luminescence (monitored at 188 nm) and emission spectrum of  $\text{Nd}^{3+}$   $5d\text{--}4f$  luminescence (under excitation at 176 nm) in  $\text{Na}_{0.4}(\text{Y}_{0.995}\text{Nd}_{0.005})_{0.6}\text{F}_{2.2}$ .



**Fig. 3.** Decay curves of  $\text{Nd}^{3+}$  5d-4f luminescence (recorded at 188 nm) in  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Nd}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.005, 0.05, 0.2, 1$ ). Excitation wavelength was 176 nm.

excited  $\text{Nd}^{3+}$  ions to neighboring non-excited  $\text{Nd}^{3+}$  ions. The concentration quenching of  $\text{Nd}^{3+}$  5d-4f luminescence appears at relatively low concentration ( $x = 0.05$ ) of  $\text{Nd}^{3+}$  (see also the decrease of luminescence intensity with  $x$  due to quenching effect in Fig. 1). The efficient cross-relaxation energy transfer occurs because of the rather rich energy level structure of excited 4f levels of  $\text{Nd}^{3+}$  which results in the existence of a set of 5d-4f radiative transitions which are quasi-resonant with corresponding absorption 4f-4f transitions.

The time-resolved emission spectra recorded for the  $\text{Na}_{0.4}(\text{Y}_{0.99}\text{Tm}_{0.01})_{0.6}\text{F}_{2.2}$  crystal in the spectral range of 160–230 nm upon  $\text{Tm}^{3+}$  4f-5d excitation are presented in Fig. 4. The spectra correspond to parity-allowed interconfiguration  $4f^{11}5d - 4f^{12}$  transitions in the  $\text{Tm}^{3+}$  ion. The slow component of  $\text{Tm}^{3+}$  luminescence with the shortest-wavelength band peaked at 175 nm is due to SF ( $\Delta S = 1$ ) 5d-4f transitions, i.e. transitions from the lowest (HS) state of  $4f^{11}5d$  configuration, with spin  $S = 2$ , to different levels of  $4f^{12}$  configuration, including the ground multiplet term  $^3\text{H}_6$ , which have the value of spin  $S = 1$  [2]. The fast component of  $\text{Tm}^{3+}$  luminescence with the shortest-wavelength band peaked at  $\sim 169$  nm is due to SA ( $\Delta S = 0$ ) 5d-4f transitions, i.e. transitions from the higher-lying LS state of  $4f^{11}5d$  configuration, which has the same value of spin ( $S = 1$ ) as the final state multiplets of  $4f^{12}$  configura-

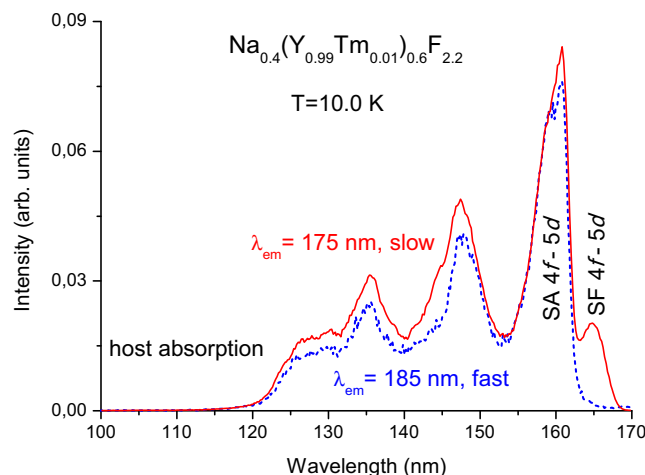


**Fig. 4.** Emission spectra of spin-allowed (fast), spin-forbidden (slow) and total 5d-4f luminescence of  $\text{Tm}^{3+}$  in  $\text{Na}_{0.4}(\text{Y}_{0.99}\text{Tm}_{0.01})_{0.6}\text{F}_{2.2}$ . The assignments of the bands to particular transitions are shown for the fast emission component. Excitation wavelength was 160 nm. The intensity of the fast component is scaled to the intensity of the slow component.

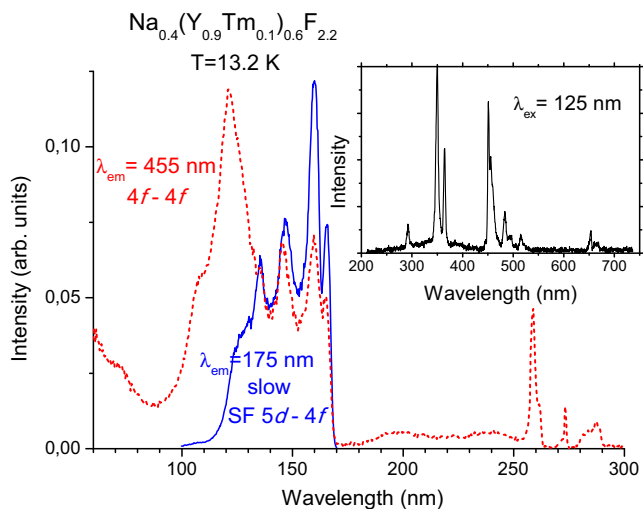
tion. The assignments of the bands corresponding to SA 5d-4f transitions are given in Fig. 4.

The excitation spectra recorded in the range of 100–170 nm for the  $\text{Tm}^{3+}$  SF (monitored at 175 nm) and SA (monitored at 185 nm) 5d-4f luminescence in the  $\text{Na}_{0.4}(\text{Y}_{0.99}\text{Tm}_{0.01})_{0.6}\text{F}_{2.2}$  crystal are shown in Fig. 5. For the measurements of excitation spectra of SA luminescence the emission band at 185 nm was selected because of better spectral separation from SF luminescence. The threshold in the excitation spectrum of SF luminescence at about 168 nm corresponds to the onset of  $4f^{12} - 4f^{11}5d$  SF absorption transitions from the ground  $4f^{12} \ ^3\text{H}_6$  state to the lowest HS 5d state of  $\text{Tm}^{3+}$ . The excitation spectrum of SF luminescence has four distinct maxima. However, only the lowest-energy band peaked at  $\sim 165$  nm corresponds to SF 4f-5d transitions. Other three higher-energy bands coincide with excitation bands of SA 5d-4f luminescence. The excitation spectrum of  $\text{Tm}^{3+}$  SA 5d-4f luminescence has the onset at  $\sim 163$  nm and the lowest-energy band peaked at  $\sim 160$  nm. The absorption coefficient for SA transitions from the ground  $4f^{12} \ ^3\text{H}_6$  state to LS 5d states of  $\text{Tm}^{3+}$  is several orders of magnitude larger than that for SF transitions. Accordingly, SF 5d-4f luminescence is excited at  $\lambda_{\text{ex}} \leq 163$  nm as a result of relaxation from the directly excited higher-lying LS 5d states to the lowest-energy HS 5d level. As one can expect, the first (lowest-energy) excitation band of SF luminescence is more pronounced for the higher concentration of  $\text{Tm}^{3+}$  (compare Figs. 5 and 6). Similar to the case of  $\text{Nd}^{3+}$ , at shorter wavelengths there is no energy transfer from the host to 5d levels of  $\text{Tm}^{3+}$ .

Excitation spectra of  $\text{Tm}^{3+}$  SF 5d-4f luminescence (monitored at 175 nm, slow component) and 4f-4f luminescence (monitored at 455 nm) in  $\text{Na}_{0.4}(\text{Y}_{0.99}\text{Tm}_{0.01})_{0.6}\text{F}_{2.2}$  are compared in Fig. 6. According to the 4f energy level structure of  $\text{Tm}^{3+}$  in fluorides [12], if one excludes from the consideration the  $^1\text{S}_0$  level having a very high energy  $\sim 75,000 \text{ cm}^{-1}$  ( $\sim 93.75$  nm), there is a group of highest-energy 4f levels ( $^1\text{I}_6, ^3\text{P}_{J=0,1,2}$ ) at some  $35,000\text{--}38,500 \text{ cm}^{-1}$  (see narrow lines in the region 250–300 nm in the excitation spectrum of 4f-4f luminescence in Fig. 6) separated from the lowest (HS) 5d level by large energy gap ( $>20,000 \text{ cm}^{-1}$ ) which prevents population of these 4f levels as a result of non-radiative relaxation from 5d level. However, 4f-4f luminescence from the lowest level of this group of 4f levels ( $^1\text{I}_6$ ) is observed under both 4f-5d absorption (for high enough concentrations of  $\text{Tm}^{3+}$ ) but mostly efficiently within the broad excitation band peaked at  $\sim 120$  nm (see insertion of Fig. 6). The latter band corresponds to transition to charge transfer ( $\text{F}^- - \text{Tm}^{3+}$ ) state [13–15] from which the non-radiative relaxation



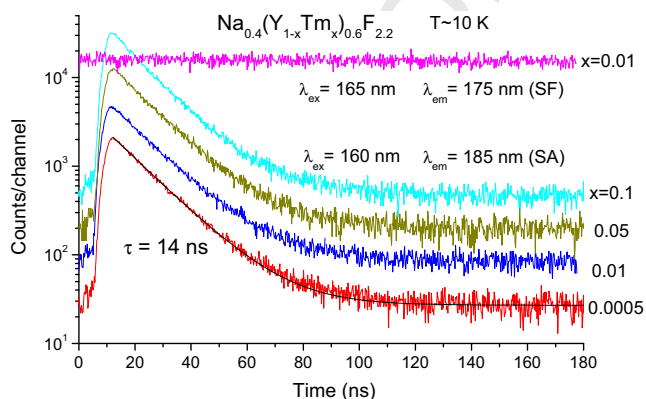
**Fig. 5.** Excitation spectra of  $\text{Tm}^{3+}$  SF (monitored at 175 nm) and SA (monitored at 185 nm) 5d-4f luminescence in  $\text{Na}_{0.4}(\text{Y}_{0.99}\text{Tm}_{0.01})_{0.6}\text{F}_{2.2}$ .



**Fig. 6.** Excitation spectra of  $\text{Tm}^{3+}$  SF 5d-4f luminescence (monitored at 175 nm) and 4f-4f luminescence (monitored at 455 nm) in  $\text{Na}_{0.4}(\text{Y}_{0.9}\text{Tm}_{0.1})_{0.6}\text{F}_{2.2}$ . Insertion shows  $\text{Tm}^{3+}$  4f-4f emission spectrum under excitation into the charge transfer ( $\text{F}^- - \text{Tm}^{3+}$ ) band at 125 nm.

populates excited 4f levels. Under 4f-5d excitation the appearance of 4f-4f luminescence is not due to some channels of non-radiative 5d-4f relaxation within the ion but occurs as a result of cross-relaxation energy transfer between the  $\text{Tm}^{3+}$  ions. In contrast to the lowest LS 5d level with nanosecond decay time, the lowest HS 5d level of  $\text{Tm}^{3+}$  has rather long lifetime and the rate of cross-relaxation from this level can compete with radiative decay (SF 5d-4f luminescence). The observed process of cross-relaxation can be described as  $(5d, {}^3H_6) \rightarrow ({}^1G_4, {}^3P_2)$ . The details of the interplay between 5d-4f and 4f-4f luminescence of  $\text{Tm}^{3+}$  can be found in [13,14] (for some other fluoride hosts). In contrast to  $\text{Tm}^{3+}$  5d-4f luminescence,  $\text{Tm}^{3+}$  4f-4f luminescence is well excited under the host absorption, similar to the results obtained earlier in [16].

Decay curves for  $\text{Tm}^{3+}$  SA and SF 5d-4f luminescence in  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Tm}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.01, 0.1, 1$ ) recorded upon 4f-5d excitation of  $\text{Tm}^{3+}$  are depicted in Fig. 7. Decay time for the slow (SF) component (detected at 175 nm) is in the microsecond range and accordingly the respective decay curve looks in the graph as a horizontal line in the working time scale. Decay time of SA luminescence is 14 ns independent of concentration (in the range of 0.05 – 10%), i.e. no concentration quenching is observed for  $\text{Tm}^{3+}$  SA 5d-4f lumines-



**Fig. 7.** Decay curves of  $\text{Tm}^{3+}$  SA (recorded at 185 nm under excitation at 160 nm) and SF (recorded at 175 nm under excitation at 165 nm) 5d-4f luminescence in  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Tm}_x)_{0.6}\text{F}_{2.2}$  ( $x = 0.0005-0.1$ ). Decay curves of SA luminescence measured for different concentrations of  $\text{Tm}^{3+}$  are shifted with respect to each other along y-axis.

cence for  $\text{Tm}^{3+}$  doping level up to 10%. This is due to the specific energy level structure of  $\text{Tm}^{3+}$  described above which makes the cross-relaxation energy transfer from LS 5d level of  $\text{Tm}^{3+}$  (leading to concentration quenching) less probable than 5d-4f radiative (plus LS-HS non-radiative) decay.

As it is clearly seen in Fig. 4 (curve ‘integral’) the relative intensity of the SA component is rather small. This means that efficient nonradiative relaxation occurs from the higher-lying LS 5d state, responsible for SA 5d-4f luminescence, to the lower-lying HS 5d state from which SF luminescence is observed. Usually it is supposed that efficient nonradiative multiphonon relaxation occurs if the gap between the levels is not more than 4–5 times larger than the cutoff phonon energy of the crystal [2]. For the system  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{RE}_x)_{0.6}\text{F}_{2.2}$  the cutoff phonon energy is expected to be similar to that in other fluoride crystals i.e. is  $\sim 500 \text{ cm}^{-1}$ . The energies of the lowest 5d levels for SA and SF luminescence in  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{Tm}_x)_{0.6}\text{F}_{2.2}$ , estimated as the crossing points between respective emission and excitation spectra, are  $\sim 60,850$  and  $\sim 59,025 \text{ cm}^{-1}$ , respectively, i.e. the energy gap between emitting 5d levels for SA and SF 5d-4f luminescence is  $\sim 1800 \text{ cm}^{-1}$ . So the efficient nonradiative multiphonon relaxation between LS and HS 5d levels of  $\text{Tm}^{3+}$  in  $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}:\text{Tm}^{3+}$  can be indeed expected.

The quantitative data on spectral and timing properties of VUV luminescence due to 5d-4f transitions of  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$  [9] and  $\text{Tm}^{3+}$  doped into  $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$  are compiled in Table 1.

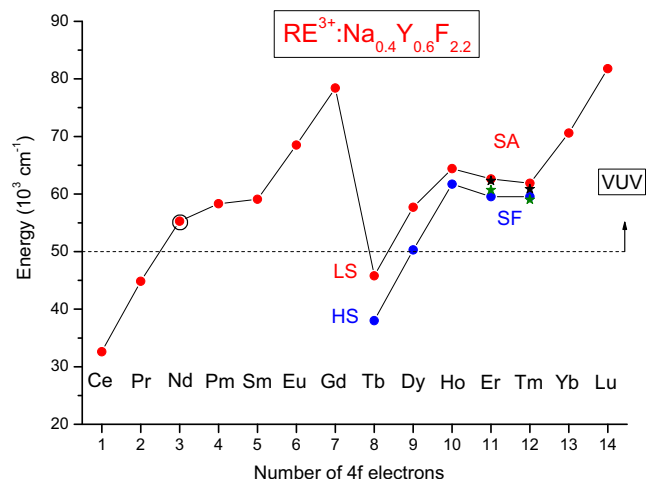
We can now construct the energy level diagram for lowest 5d levels of all  $\text{RE}^{3+}$  ions in this complex fluoride system using well-known methodology of P. Dorenbois [17] if we take as the basis, for example, the experimental energy of 5d level for  $\text{Nd}^{3+}$  ion (Fig. 8). As one can see in the figure, the energies of the lowest HS and LS 5d levels calculated for  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  according to this methodology show satisfactory agreement with experimental values.

The  $\text{Na}_{0.4}(\text{Y}_{1-x}\text{RE}_x)_{0.6}\text{F}_{2.2}$  ( $\text{RE}^{3+} = \text{Nd}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}$ ) systems can be considered as possible active media for VUV solid-state lasers with optical pumping. The absorption coefficient for SA 4f-5d transitions is of the order of  $100 \text{ cm}^{-1}$  for a concentration of ions about 1%. So, the conditions for direct optical pumping (e.g. by rare gas discharge radiation) of  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$  or  $\text{Tm}^{3+}$  doped crystals are acceptable. On the other hand, the upconversion (two-photon) pumping via some intermediate 4f level can be also considered. For example, upconversion excitation of  $\text{Nd}^{3+}$  5d-4f luminescence can be well realized by XeF (351/353 nm) or KrF (248 nm) laser via intermediate  ${}^4D_{5/2,3/2}$  and  ${}^2F(2)_{7/2}$  4f levels respectively [18,19]. Upconversion excitation of  $\text{Er}^{3+}$  5d-4f luminescence is possible by using ArF laser (193 nm) via intermediate  ${}^2H(1)_{11/2}$  4f level [19]. Unfortunately there are no excited 4f levels of  $\text{Tm}^{3+}$  suitable for upconversion excitation to 5d levels using excimer lasers. From the viewpoint of possible VUV laser schemes the SF 5d-4f transitions of  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions are more suitable as laser transitions.

**Table 1**

Parameters of SA and SF 5d-4f luminescence of  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  ions in the  $\text{Na}_{0.4}\text{Y}_{0.6}\text{F}_{2.2}$  host. The data presented are taken for samples with doping concentrations of 0.5% for  $\text{Nd}^{3+}$  and 1.0% for  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$ ;  $\lambda_{\text{em}}$  are peak wavelengths of the luminescence bands;  $\lambda_{\text{ex}}$  are peak wavelengths of the first bands of the excitation spectra;  $E_{\text{ZPL}}$  are the energies of the lowest LS and HS 5d levels estimated as the crossing points between 5d-4f emission and 4f-5d excitation spectra for SA and SF 5d-4f luminescence, respectively;  $\tau$  are luminescence decay times. Data for  $\text{Er}^{3+}$  are taken from [9].

Ion	$\text{Nd}^{3+}$	$\text{Er}^{3+}$		$\text{Tm}^{3+}$	
		SA	SF	SA	SF
$\lambda_{\text{em}}$ (nm)	182.5	164.8	167.8	169.0	174.8
$\lambda_{\text{ex}}$ (nm)	175.5	156.5	163.0	160.8	164.8
$E_{\text{ZPL}}$ ( $\text{cm}^{-1}$ )	55,295	62,305	60,680	60,850	59,025
$\tau$ (ns)	16.5	11	560	14	>1000



**Fig. 8.** The energies of the lowest  $4f^{n-1}5d$  levels of  $RE^{3+}$  ions in the fluoride system  $Na_{0.4}Y_{0.6}F_{2.2}:RE^{3+}$ . 'Filled circles' are the energies calculated according to [15] if one takes the experimental energy of the lowest  $5d$  level for the  $Nd^{3+}$  ion as the basis. The 'stars' are the experimental energies obtained for  $Er^{3+}$  (from [9]) and  $Tm^{3+}$  (this work).

In such a scheme the optical pumping can be realized on the strong SA  $4f-5d$  transitions and the upper laser level (the lowest HS  $5d$  level responsible for SF luminescence) will be populated via fast nonradiative relaxation from a higher-lying LS  $5d$  level. As a result, the Stokes shift of laser transition from the edge of strong SA  $4f-5d$  absorption is rather large and reabsorption effect is small. This introduces an advantage for  $Er^{3+}$ - and  $Tm^{3+}$ -based laser schemes compared to  $Nd^{3+}$ -based one.

#### 4. Conclusions

The time-resolved low-temperature ( $T \sim 10$  K) VUV spectroscopy studies of  $5d-4f$  luminescence of  $Nd^{3+}$  and  $Tm^{3+}$  ions in the fluoride systems  $Na_{0.4}(Y_{1-x}RE_x)_{0.6}F_{2.2}$  ( $RE^{3+} = Nd^{3+}, Tm^{3+}$ ) have been performed with synchrotron radiation excitation. The emission and excitation spectra as well as luminescence decay curves were measured for the wide range of doping concentrations. Remarkable concentration quenching is observed for  $Nd^{3+}$   $5d-4f$  luminescence whereas SA  $5d-4f$  luminescence of  $Tm^{3+}$  possesses no concentration quenching (tested for doping level up to 10%). On the other hand, the fast SA  $5d-4f$  luminescence of  $Tm^{3+}$  is rather weak, i.e. there exists efficient non-radiative relaxation from higher lying  $5d$  states to the lowest HS  $5d$  level responsible for SF  $5d-4f$  luminescence. These fluoride systems can be considered as promising active media for VUV solid state lasers with optical pumping.

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