VUV spectroscopy of wide band crystals doped with rare earth (RE) ions is one of the challenging field of solid state physics, that arise from several applications for materials with optical activity in the VUV range [1]. An important problems of RE spectroscopy in VUV range is identification of transition involving 4f\(n-1\)5d states in excitation and emission spectra. In this work a VUV spectroscopic research for Nd\(^{3+}\) and Tm\(^{3+}\) ions in SrF\(_2\) crystals have been performed. The crystals for research were grown by the Stokbarger technique at Pyshinsky technique at Pyshminsky plant GIRETMET (Russia). The experiments at 8-10 K were made at the SUPERLUMI station at HASYLAB. In VUV range the measurements of emission spectra and decay kinetics were performed with a 0.5 m Pouey-type monochromator (resolution of 10 Å) equipped with a photomultiplier R6836 for spectral measurements and with a microsphere plate detector for decay measurements. For detection of emission in visible range an ARC Spectra Pro-308i spectrograph equipped with a photomultiplier R6358P were used. The excitation spectra were corrected for the wavelength-dependent intensity variation using sodium salicylate. The emission and excitation spectra Nd\(^{3+}\) ions in SrF\(_2\):1%Nd\(^{3+}\) are presented in Fig. 1. In order to exclude the parity-forbidden 4f\(^3\)→4f\(^2\)5d transitions, these spectra were measured in the “fast” time window \(\Delta t = 11\) ns delayed with respect to the arrival of synchrotron radiation pulse on \(\delta t = 25\) ns. In emission spectrum the relatively broad bands are connected with the parity-allowed 4f\(^2\)5d→4f\(^3\) transitions of the Nd\(^{3+}\) ions (the assignments for all emission bands are shown in the figure). A Stark splitting of the transitions in multiplets is not individually resolved in the spectrum in spite of sufficiently high spectral resolution. Upon direct 4f\(^3\)→4f\(^2\)5d excitation the decay time for main band of 4f\(^2\)5d→4f\(^3\) emission at 180 nm emission equals to \(\tau \sim 14\) ns (Fig. 1, b).

The excitation spectrum of 4f\(^2\)5d→4f\(^3\) emission (182 nm) for Nd\(^{3+}\) in SrF\(_2\):1%Nd\(^{3+}\) crystals consists of several peaks in the range of 125-180 nm (denoted by A, B…, F letters on the figure). The beginning of transitions to the low-energy crystal-field component 4f\(^2\)5d (\(^{2E}\)) is presented as the onset in the excitation spectra at 180 nm (A), the transitions to the high-energy crystal-field \(^2T_2\) levels can be observed at 130-135 nm (F). A complicated structure in the range 138-173 nm (bands B, C, D, and E) may be assigned to the Coloumb interaction of 5d electron and 4f\(^2\) core.

The Tm\(^{3+}\) ions belong to the heavy lanthanide group (n > 7), for which spin-allowed and spin-forbidden 4f\(^{n-1}\)5d→4f\(^n\) transitions connected with low spin (LS) and high spin (HS) states of 4f\(^{n-1}\)5d configuration correspondingly can be observed in the spectra [2]. The VUV-emission spectrum of SrF\(_2\):1%Tm\(^{3+}\) upon direct f-d excitation is shown in Fig. 2 and consists of slow
luminescence component only (the decay time in microsecond range). This emission bands is connected with the spin-forbidden transition from quintet \((2S + 1 = 5)\) \(4f^{11}5d(HS)\) state to the levels of \(4f^{12}\) (the assignments are given in the figure). No emission from a LS triplet state \((2S + 1 = 3)\) of \(4f^{11}5d\) configuration is observed. It can be caused by a small energy separation of the LS and HS states that makes multi-phonon non-radiative relaxation highly probable.

Figure 2: SrF\(_2\):1\%Tm\(^{3+}\), \(T = 8\) K. Emission spectra upon f-d excitation at 155 nm (1); excitation spectra for the \(4f^{11}5d(HS)\) \(\rightarrow 3H_6\) emission at 167 nm (2) and for \(^1G_4 \rightarrow 3H_6\) emission at 451 nm (3).

Energy level structure of the \(4f^{11}5d\) configuration is observed in the excitation spectra for d-f emission at 166 nm (Fig. 2, curve 2). The bands with maxima at 155 (A), 141 (B) and 132 nm (C) can be assigned to the transitions to the \(4f^{11}5d(\ell = 2)\) crystal-field levels. For designation of the bands subjected to the Coulomb interaction we used the same notation as authors [3]. So the bands lettered A, B, C coupled to the lowest states of \(4f^{11}\) core can be written as \(2E(4I_{15/2}), 2E(4I_{13/2}), 2E(4I_{11/2})\) states. The transitions to the high-energy \(2^1T_2\) states are not revealed in the spectrum due to competition with the host absorption. The lowest-energy spin-forbidden \(^3H_6 \rightarrow 4f^{11}5d(HS)\) transition is observed at 162 nm.

The excitation spectrum for \(4f^{12}(^1G_4) \rightarrow 4f^{12}(^3H_6)\) emission at 451 nm has most intensity in broad bands centered at 159, 146, 136, 128 nm and in such a way demonstrates an opposite behavior with respect to excitation spectrum for d-f emission. An analogous mutual behavior of the spectra we already observed earlier for Er\(^{3+}\) ions in SrF\(_2\) crystal [4, 5]. It has to be mentioned that such behavior of excitation spectra for f-f emission in comparison with those for d-f emission in the range \(4f^{n} \leftrightarrow 4f^{n-5}d\) absorption is not always observed for RE ions in other matrixes, see for example [6]. The observed phenomena reflects partly the variation of absorption coefficient in the transparency range and the competition in the energy transfer processes to the emitting levels of \(4f^{n}5d\) and \(4f^{n}\) configurations. It can be assumed that there is increased probability of spin-forbidden f-d transitions. As results the f-f emission is effectively enough excited at all possible levels of \(4f^{11}5d\) configuration. The opposite behaviour of excitation spectra for f-f and d-f emission is observed because intensity of f-f emission is decreased under excitation at spin-allowed states since a most probable way for relaxation of such states is so-called non-radiative intersystem crossing, which populates the low-energy emitting HS state.

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References