

VUV spectroscopy of rare earth doped complex fluoride crystals

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During recent years applications like new efficient phosphors for plasma display panels and mercury free luminescent lamps as well as search for fast scintillators and laser hosts in VUV has been driving force for extensive spectroscopic investigation of rare-earth doped materials. In order to design material with expected performance knowledge about all kind of energy relaxation processes and their dynamics is required. Using tunable synchrotron radiation in VUV we have been studying energy relaxation in Er^{3+} doped LiYF_4 and BaY_2F_8 single crystals as well as in LiKGdF_5 and LiKYF_5 hosts doped with Er^{3+} and co-doped with Dy^{3+} ions [1-3]. After Er^{3+} f-d excitation, radiative cascades and cross-relaxations populating lower-lying f-levels were observed. In the case of f-d excitation of Er^{3+} doped LiKGdF_5 at room temperature, the d-f emission was practically quenched and an enhancement of UV/visible emissions was observed [2]. Cross-relaxation processes and energy transfer occurring in these co-doped systems make them promising materials for down-conversion phosphors as shown in [4]. In the present contribution we report on the influence of doping concentration (up to the stoichiometric BaEr_2F_8 and LiErF_4 crystals) and temperature (300 and 10 K) on the spectral properties, energy relaxation and transfer processes in the above mentioned crystals.

The crystals doped with Er^{3+} ions of various concentrations were grown by the vertical Bridgeman [5] (BaY_2F_8) and Czochralski (LiYF_4) methods and those co-doped with Dy^{3+} by the hydrothermal technique (LiKGdF_5 and LiKYF_5) [6]. The luminescence experiments under excitation by VUV synchrotron radiation in the range of 4-15 eV were carried out at the SUPERLUMI station of HASYLAB at DESY [1]. Polished plates of crystals were mounted on the sample holder of a flow type He cryostat ($T=6-300$ K). In the visible-UV range, excitation spectra were recorded with a PMT (Hamamatsu, R6358P) while emission spectra with higher resolution were measured by means of a liquid nitrogen cooled CCD camera (Princeton Instruments) mounted on the second exit arm of a 0.3 m monochromator-spectrograph SpectraPro308 (Action Research). Emission and excitation spectra in VUV were recorded with a 0.5 m Pouey type monochromator equipped with a solar-blind PMT (Hamamatsu R6838).

Depending on the host material and the respective rare earth ion the interconfigurational spin-allowed and forbidden 5d-4f as well as intra-

configurational 4f-4f radiative transitions are observable. Along with f-f transitions in the UV-visible (for example strong emission lines from the ${}^2\text{P}_{3/2}$ and ${}^4\text{S}_{3/2}$ at 400 and 550 nm, respectively) region we detected the coexisting spin-allowed and forbidden 5d-4f transitions of Er^{3+} in LiYF_4 (156 and 166 nm, the dominant emission lines), BaY_2F_8 (161 and 170 nm), BaEr_2F_8 (161 and 170 nm), LiKYF_5 (162 and 169.5 nm). The weak d-f emission in LiErF_4 (156 nm) arises from the spin-allowed transition. Also weak spin-allowed d-f emission of Er^{3+} in LiKGdF_5 (162 nm) was detected at 10 K whereas it is practically quenched at RT in agreement with Makhov et al. [2].

The higher lying 4f-levels located just below the 5d bands can play an important role in the non-radiative relaxation from the latter states. Subsequent radiative and/or cross-relaxation processes depopulate these energetically well-separated high 4f states enhancing particular 4f emissions. It is well known that the energetic positions of d-bands depend sensitively on the host whereas 4f levels are practically not influenced. For example, in $\text{LiYF}_4:\text{Er}$ at 10 K the 4f ${}^2\text{F}(2)_{5/2}$ state is just above the lowest d-band resulting in the different excitation onsets for emissions starting from the ${}^2\text{P}_{3/2}$ and ${}^4\text{S}_{3/2}$ states in the region of 4f-5d transitions (see [1]). The former state is populated via cross-relaxation while the excitation of the latter one results from a radiative cascade. In $\text{BaY}_2\text{F}_8:\text{Er}$ the both lowest d-bands are below the 4f ${}^2\text{F}(2)_{5/2}$ state and the emission from the ${}^2\text{P}_{3/2}$ state starts only after excitation into higher d-states, while the onset of the ${}^4\text{S}_{3/2}$ emission coincides with the lowest f-d transition [3]. These relaxation processes will be discussed for Er doped LiYF_4 and BaY_2F_8 crystals. Because of the increasing probability of cross-relaxation with rising doping concentration a considerable redistribution of intensities of f-f emissions and changes in the luminescence spectra are observed. On the basis of experimental data obtained under VUV excitation the radiative and non-radiative relaxation processes of Er^{3+} ions in complex fluorides will be discussed, including peculiarities of energy relaxation and transfer processes in co-doped (Er^{3+} , Dy^{3+}) LiKGdF_5 crystals at 10 K.

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