Luminescent properties of solid solutions
Lu$_x$Y$_{1-x}$PO$_4$, undoped and doped with Ce$^{3+}$ and Eu$^{3+}$

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Phosphates doped with rare-earth ions are considered as promising materials for scintillating detectors, X-ray imaging and plasma display panels [1]. Enhancement of the light yield is one of actual problems for scintillating detectors and sometimes it can be achieved by using solid solutions. Previously it was shown that superior light yield is observed for the perovskite solid solutions Lu$_x$Y$_{1-x}$AlO$_3$:Ce in comparison with YAP:Ce or LuAP:Ce [2]. Enhancement of luminescence intensity under X-ray excitation has been also detected for Lu$_2$Sc$_{1-x}$BO$_3$:Ce$^{3+}$ [3] and Lu$_x$Y$_{1-x}$BO$_3$:Eu$^{3+}$ [4]. Here we studied the luminescence properties of a series of phosphate solid solutions with general formula Lu$_x$Y$_{1-x}$PO$_4$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1$), undoped as well as doped with 0.5 mol % Eu$^{3+}$ or with 0.5 mol % Ce$^{3+}$. Samples were synthesized by sol-gel method. Measurements were performed using synchrotron radiation in the energy region 3.7-22 eV and temperature region 10 – 300 K at the SUPERLUMI station, DESY [5].

Undoped samples demonstrate complex structure of the emission spectrum (fig.1). Up to three emission bands in the UV and blue spectral regions were observed under selective excitation. Excitation spectra for these bands substantially differ, implying different origin of the centers responsible for these emission bands. However all these spectra demonstrate a common feature, namely a sharp drop of intensity in the 9 eV. It allows ascribing these bands to the emission centers related to the defects of the crystal structure. The energy transfer from the host states, which are excited at $E_{ex}$ > 9 eV, is not efficient and therefore determines the observed decrease of intensity. The threshold shifts by ~0.5 eV to the higher energies when Y ions are completely substituted with Lu, that indicates the increase of the bandgap with the increase of x value.

For the doped samples the observed luminescence spectra demonstrate characteristic emission on 4f-4f transitions in Eu$^{3+}$ doped samples (sharp lines in the spectral region 580 – 720 nm, see fig.2) and on 5d-4f transitions in Ce$^{3+}$ doped samples (two broad bands at 335 and 360 nm). The structure of the spectrum related to Eu$^{3+}$ does not change for all samples that indicate the absence of second phase in the samples, which was a significant problem for the solid solutions of borates [4]. Excitation spectra of samples doped with Eu$^{3+}$ demonstrate low-intensity sharp lines in the energy region below 4.5 eV that arise due to the electronic transitions within 4f shell of Eu$^{3+}$. Broad band peaking at 5.8 eV is ascribed to the charge transfer transitions from oxygen to Eu ions. In the energy region slightly below the fundamental absorption region two sharp peaks are observed at 8.15 eV and 8.75 eV (see fig.3 for the sample with $x = 0.9$). The first one is tentatively ascribed to the f-d intracenter transitions in Eu$^{3+}$, while the second one – to the creation of excitons. The intensity of emission of Eu$^{3+}$ is enhanced for the intermediate values of x (see inset to fig. 2) and demonstrate maximum at $x = 0.7$ for the case of intracenter excitation. Energy transfer efficiency from the host to Eu$^{3+}$ ions is also increasing for the intermediate values of x as it follows from the fig.4. Actually the intensity in the excitation spectrum of the sample with $x = 0.5$ is higher than for the samples with $x = 0.3$ and 0.9. It may indicate the constraint of the thermalization length of the hot charge carriers that lead to the enhanced probability for generic electron-hole pairs to be captured by the emission center. Clusterization of the solid solution has been proposed as a possible reason for the constraint [2]. The typical excitation spectrum for the samples doped with Ce$^{3+}$ is presented in fig.3 (curve 3). In the transparency region distinct peaks were observed that are due to the 4f – 5d transitions in Ce$^{3+}$. In the region of exciton creation, the spectrum demonstrates local minimum that is followed with the gradual increase of intensity with further increase of excitation energy. It implies that the energy transfer to Ce$^{3+}$ centers occurs through the consecutive capture of holes and electrons (i.e. recombination mechanism) while energy transfer to Eu$^{3+}$...
centers is also possible with the prior creation of the excitons (excitonic mechanism). The dependence of the Ce$^{3+}$ emission intensity on the x value will be the subject of our further studies.

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References