Luminescence Study of the Gadolinium and Lutecium Borates and Phosphates Doped with Ce$^{3+}$ and Tb$^{3+}$

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Searching for the new scintillating materials suitable for the ionizing radiation registration is still the actual problem. Recently it was shown that oxides doped with rare-earth elements can be considered for such applications [1]. High light yield and spatial resolution are important parameters for the detector. Application of the matrix scintillators composed with the crystals of submicron dimensions will allow to obtain the spatial resolution not worth than 10 µm. This background motivated us to perform the systematic experimental study of the set of scintillating oxide materials with submicron dimensions.

The luminescence properties of the GdPO$_4$, LuPO$_4$, GdBO$_3$ and LuBO$_3$ doped with Ce$^{3+}$ and Tb$^{3+}$ ions were studied. The investigated materials were synthesized by sol-gel method and characterized by the X-ray diffraction and scanning electron microscopy. Predominant size of the obtained crystalline particles is in the range of 250–670 nm. Luminescence spectra in the wavelength region of 200 – 900 nm at UV and VUV excitation as well as luminescence excitation spectra in the energy region 4 – 25 eV were measured using synchrotron radiation (SR) at the Superlumi station (DESY, Hamburg) [2].

Luminescence of LuBO$_3$:Ce (0.5 mol %) as well as its decay spectra and luminescence excitation are presented in fig.1. This compound is known as scintillator with high light yield 26000 - 27000 ph/MeV. Light yield of LuBO$_3$:Ce crystallized in the vaterite phase exceeds those crystallized in calcite phase [1]. X-ray phase analysis showed that the measured sample was crystallized in the vaterite phase with presence of the calcite phase (< 4 mass %). Two luminescence bands of Ce$^{3+}$ were observed at 390 and 420 nm. Decay curves were measured at different excitation energies. Fast decay with the decay time 55 ns was observed at $E_{\text{ex}}$ = 7.75 eV. Slow decay components appear at the lower (5.16 eV) and higher (10.8 eV) excitation energies. In the latter case luminescence rise-on is also observed. It may be due to the energy transfer from the matrix to the cerium dopant as the 10.8 eV exceeds the bandgap value of LuBO$_3$. Presence of the slow decay component at low-energy excitation $E_{\text{ex}}$ = 5.26 eV may be due to the overlapping of cerium intracenter excitation states with defect states. Luminescence excitation spectra are presented for the measurements in the fast (2.5 - 20 ns after the excitation pulse of the synchrotron radiation) and slow (90 - 150 ns) time windows. The intensity of the spectra is normalized. The main difference between the spectra measured in the fast and slow time windows is observed in the region of the peak at 7.8 eV. The energy position of the peak is too high to assign it to the intracenter transitions in Ce$^{3+}$ ion. According to [1] the bandgap of LuBO$_3$ is 7.0
eV for the vaterite phase. We suppose that prevailing of the fast component in the excitation peak at 7.8 eV is due to the resonance energy transition from the exciton formed on the edge of the fundamental absorption region to the Ce\(^{3+}\) luminescence center. Similar behavior was observed in the exciton energy region for LuAlO\(_3\):Ce in [3]. In this case the bandgap value can be estimated on the high-energy minimum of the peak were the relative contribution of slow component significantly increases as \(E_g \sim 8.4\) eV.

Luminescence of Tb\(^{3+}\) - doped compounds is presented for the gadolinium borates in fig.2. Samples were prepared by a mineral sol-gel method. Gel sedimentation was controlled by continuous measurement of pH. Gel samples were divided by pH value at 5.0 and 7.0. The obtained samples were characterized by X-ray powder diffraction and scanning electron microscopy. It is found that in the pH interval from 5.0 to 7.0 the ratio of meta- and ortho- borate phases appropriately changes from 70\%\(\text{Gd(BO}_2\text{)}_3\):30\%\(\text{GdBO}_3\) at pH=5.0 to 100\%\(\text{GdBO}_3\) at pH=7.0. Luminescence spectra are represented with four non-elemetary luminescence bands in the wavelength regions 480 – 500, 535 – 560, 580 – 595 and 615 – 635 nm that are due to the \(^5\text{D}_3 \rightarrow ^7\text{F}_J\) (\(J = 3-6\)) transitions in Tb\(^{3+}\)-ions. Position and relative intensity of the luminescence peaks significantly depend on the sample. The discrepancy is due to the different symmetry of the oxygen ions surrounding of terbium ions in different phases of gadolinium borate. The integrated luminescence intensity of orthoborate phase (pH = 7.0) is slightly higher than that of the mixture of the meta- and ortho-borate phases (pH = 5.5) at band-to-band excitation. In the inset of the fig.2 integrated luminescence intensities of the investigated samples are presented. Luminescence intensity of all investigated borates and lutetium phosphate exceeds that of the well-known scintillating crystal zinc tungstate. The highest luminescence intensity was detected for the LuBO\(_3\):Tb (5 mol\%) that exceeds the luminescence of LuBO\(_3\):Ce (0.5 mol\%) in 1.5 times and ZnWO\(_4\) in 6.4 times.

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References