In the present report we present the results of investigation of luminescence properties for nanosized LaPO\(_4\):Ce,Tb (LPO) which nowadays is one of the most promising highly luminescent phosphors and one of the best candidates for biomedical applications such as fluorescence resonance energy transfer assays, biolabelling, optical imaging, or phototherapy. For bulk LPO it is well known [1] that intensive Tb\(^{3+}\) luminescence arises under UV excitation of Ce\(^{3+}\) ion (4f\(_1\)→4f\(_0\)5d\(_1\) transition). After energy transfer from Ce\(^{3+}\) to Tb\(^{3+}\) a green Tb\(^{3+}\) emission resulting from 5D\(_4\)→7F\(_J\) relaxation takes place. The energy transfer mechanism between Ce\(^{3+}\) and Tb\(^{3+}\) ions is not clear so far, however many authors believe that a resonant energy transfer from Ce\(^{3+}\) to Tb\(^{3+}\) occurs. On the other hand, in many cases for successful realization of a resonant energy transfer it is necessary that the spectrum of the excitability of Tb\(^{3+}\) should overlap strongly with a Ce\(^{3+}\) decay. According to literature data [2, 3] Ce\(^{3+}\) emission band does not overlap with 4f\(_8\)→4f\(_8\) absorption of Tb\(^{3+}\) in LPO and, therefore, resonant energy transfer processes seem improbable. To our knowledge there are not reliable data about energy transfer processes in nanosized LPO. Therefore, the detailed investigation of luminescence properties in nanosized LPO was performed in the current study using luminescence spectroscopy technique in visible-VUV spectral range.

Luminescence measurements were carried out using pulsed synchrotron radiation at the SUPERLUMI station [4, 5] at HASYLAB (DESY, Hamburg). In the present study LaPO\(_4\):Ce,Tb (45 mol.\%, 15 mol.\%) nanopowder (particle size 10-15 nm) was produced by a microwave-induced synthesis in ionic liquids. This method is described in detail in [6, 7]. The commercial (micro sized) bulk LaPO\(_4\):Ce,Tb phosphor (from Philips) was also studied in the present work for comparison.

Figure 1: Emission spectra of commercial and nanosized LaPO\(_4\):Ce,Tb under excitation in Ce\(^{3+}\) absorption band (250 nm) (in the center). The spectra consists on two main well-distinguished parts: broad 4f\(_1\)→4f\(_0\)5d\(_1\) Ce\(^{3+}\) emission band peaking at ~340 nm and sharp Tb\(^{3+}\) lines in the green to red spectral range. The spectra Ce\(^{3+}\) emission are depicted in detail on the left picture, whereas one of the Tb\(^{3+}\) line is shown on the right picture for both sample in order to demonstrate the lines fine structure.

Luminescence spectra as well as luminescence excitation spectra are depicted on the Fig. 1-3 for both nanosized and bulk LPO samples. The main results obtained can be summarized as follows:

- The position and shape of the Ce\(^{3+}\) emission band are different for bulk and nanosized LPO samples (Fig. 1). On the other hand, fine structures of Tb\(^{3+}\) lines, which are well resolved in the bulk sample, are smoothed significantly in the nanosized sample.
• The low energy part of the excitation spectra for both Ce\(^{3+}\) and Tb\(^{3+}\) emissions (Fig. 2-3 left) are different for bulk and nanosized LPO. It means that energy transfer processes could be different for bulk and nanosized LPO.

• In contrast to bulk material where multiplications of electronic excitations were observed, in nanosized LPO sample the Ce\(^{3+}\) as well as Tb\(^{3+}\) emission practically are not excited if the excitation energy is higher than 10 eV (Fig. 2-3 right).

Figure 2: Excitation spectra of Tb\(^{3+}\) emission (542 nm) for commercial bulk and nanosized LaPO\(_4\):Ce,Tb at low temperature. The spectra in wide spectral range are depicted on the right picture, whereas the low energy part is shown in detail on the left one.

Figure 3: Excitation spectra of Ce\(^{3+}\) emission (340 nm) for commercial bulk and nanosized LaPO\(_4\):Ce,Tb at low temperature. The spectra in wide spectral range are depicted on the right picture, whereas the low energy part is shown in detail on the left one.

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References