

Luminescence of nano- and macrosized $\text{LaPO}_4\text{:Ce,Tb}$ excited by synchrotron radiation

Vladimir Pankratov, Anatoli I. Popov, Aleksei Kotlov¹, Claus Feldmann²

Institute of Solid State Physics, University of Latvia, Latvia

¹*HASYLAB at DESY, Hamburg, Germany*

²*Institute of Inorganic Chemistry, Karlsruhe Institute of Technology (KIT)*

Lanthanum phosphate (LaPO_4), also known as monazite, has been widely used as a phosphor and proton conductor as well as in sensors, lasers, ceramic materials, catalysts and heat-resistant materials. This is due to its interesting properties such as very low solubility in water, high thermal stability, high index of refraction, and so on [1, 2]. Trivalent cerium (Ce^{3+}) and terbium (Tb^{3+}) co-activated LaPO_4 ($\text{LaPO}_4\text{:Ce,Tb}$) bulk powder is known as most efficient because of the high-efficiency energy transfer between Ce^{3+} and Tb^{3+} [1, 3].

In the present study $\text{LaPO}_4\text{:Ce,Tb}$ (45 mol% of Ce^{3+} , 15 mol% of Tb^{3+}) nanopowder was produced via a microwave-accelerated synthesis in ionic liquids. Luminescence properties of $\text{LaPO}_4\text{:Ce}^{3+},\text{Tb}^{3+}$ in the UV–VUV spectral range were studied with pulsed synchrotron radiation from the DORIS III storage ring at DESY.

Luminescence spectra of Tb^{3+} emission for both bulk and nanosized samples are pictured in Fig. 1. In both samples the characteristic Tb^{3+} lines resulting from $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions occur. However, a significant discrepancy between emission spectra is observed if the fine structures of the Tb^{3+} emission lines are considered in details. The comparison of the fine structures of the most intensive line ($^5\text{D}_4 \rightarrow ^7\text{F}_5$) is shown as an inset in Fig. 1. In contrast to the commercial bulk material the fine structure of the Tb^{3+} lines is significantly smoothed in the case of the nanopowder.

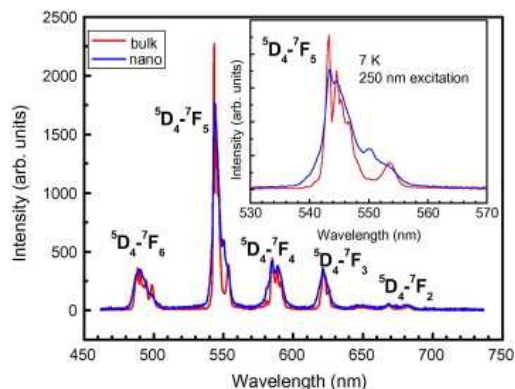


Fig. 1. Emission spectra of Tb^{3+} ions in the macroscopic and nanosized $\text{LaPO}_4\text{:Ce,Tb}$ under excitation in Ce^{3+} absorption band (250 nm).

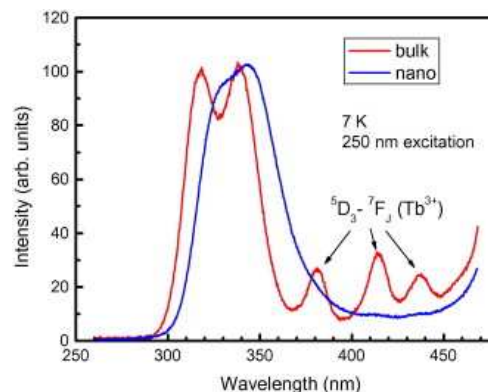


Fig. 2. Emission spectra of Ce^{3+} ions in the macroscopic and nanosized $\text{LaPO}_4\text{:Ce,Tb}$ under excitation in Ce^{3+} absorption band (250 nm).

On fig. 2 could see a significant discrepancy between commercial and nanosized $\text{LaPO}_4\text{:Ce,Tb}$ in the emission spectra of Ce^{3+} . Firstly, a characteristic duplet structure of the Ce^{3+} emission band in the 300–360 nm range caused by splitting $4f$ ground level is well resolved in the bulk sample, whereas this duplet structure is almost absent in the spectrum of the nanopowder. Secondly, the Ce^{3+} emission band is slightly shifted to the low energy side.

Excitation spectra of Ce^{3+} and Tb^{3+} are depicted in (Fig. 3) and (Fig. 4) for the bulk and the nanosized samples, respectively. The excitation spectrum of the Ce^{3+} emission in the 4.0–6.5 eV range of the bulk sample (Fig. 3) shows $4f-5d$ transition of Ce^{3+} ion in the LaPO_4 matrix. This spectrum is composed of five bands peaking at 4.46, 4.76, 5.2, 5.8 and 6.05 eV, which are due to

the transition from the ground state $^2F_{5/2} (4f^1)$ to the five crystal-field split levels of $^2D (5d^1)$ excited state in LaPO_4 lattice.

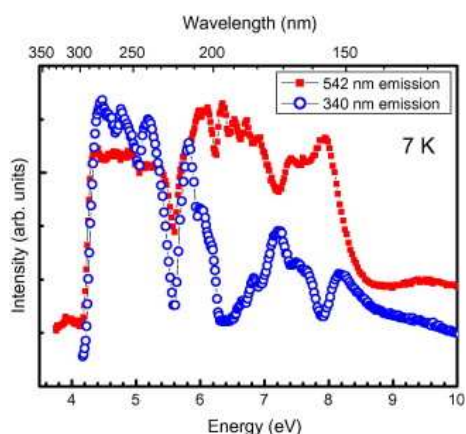


Fig. 3. Excitation spectra of Ce^{3+} (340 nm) and Tb^{3+} (542 nm) emissions in the macroscopic $\text{LaPO}_4:\text{Ce},\text{Tb}$ at 7 K.

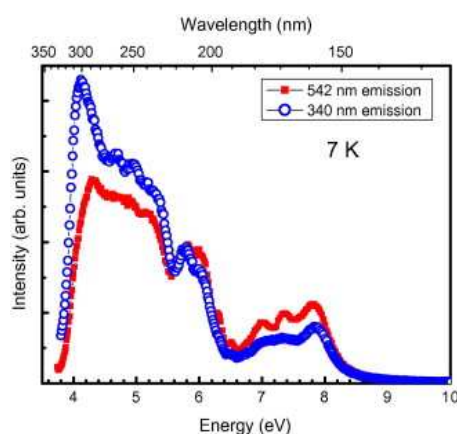


Fig. 4. Excitation spectra of Ce^{3+} (340 nm) and Tb^{3+} (542 nm) emissions in the nanosized $\text{LaPO}_4:\text{Ce},\text{Tb}$ at 7 K.

The excitation spectrum of Tb^{3+} emission for the bulk sample could be visually divided in two ranges: 4.0–5.6 eV and 5.6–7.7 eV. The excitation spectrum of Tb^{3+} emission at energies higher than 5.6 eV represents f–d transitions of the Tb^{3+} ion. The abundant structure of this part of the Tb^{3+} excitation spectrum is explained by the spin-allowed and the spin-forbidden f–d transition from the ground $^7F (4f^8)$ state to the lowest $^7D (4f^75d)$ and to the lowest $^9D (4f^75d)$ terms.

The excitation spectrum for Ce^{3+} emission in the nanosized sample has intensive bands in the 3.5–6.5 eV spectral range (Fig. 4) which are qualitatively similar to the corresponding excitation bands obtained for the bulk material in Fig. 3. However, the fine structure due to the crystal-field splitting is poorly resolved for the nanomaterial. The intensive excitation band peaking at 4.0 eV (300 nm) is observed for the nanomaterial and which is absent in the excitation spectrum of bulk $\text{LaPO}_4:\text{Ce},\text{Tb}$. We can speculate that this excitation band arises due to perturbation of the 5d levels on Ce^{3+} in nanosized $\text{LaPO}_4:\text{Ce},\text{Tb}$. As a result, 5d excited state are slightly shifted and, thus, Ce^{3+} excitation and emission spectra of the nanomaterial are shifted to the low energy side as compared to the corresponding spectra of the bulk sample.

The structure of the excitation spectrum of the Tb^{3+} emission coincides qualitatively with the shape of the excitation spectrum related to Ce^{3+} in nanosized $\text{LaPO}_4:\text{Ce},\text{Tb}$ (Fig. 4). The intensive excitation of Tb^{3+} in 3.5–5.6 eV range is due to energy transfer from Ce^{3+} . On the other hand, the part of the excitation spectrum due to f–d transitions on Tb^{3+} (5.6 eV and higher) is significantly suppressed in the nanomaterial, it means that Tb^{3+} practically cannot be directly excited in nanosized $\text{LaPO}_4:\text{Ce},\text{Tb}$, but could be excited after energy transfer from Ce^{3+} only. We suggest that due to the small nanoparticle size and a high impurity concentration, Tb^{3+} and Ce^{3+} ions are closely distributed. Since the cerium concentration is in three times higher than for terbium, Ce^{3+} ions “shield” Tb^{3+} ions and Ce^{3+} excitation is much more probable.

References

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Acknowledgment

The experiments at DESY leading to these results have received funding from European Community’s Seventh Framework Programme (FP7/2007-2013) under Grant agreement #226716.

The work of V. Pankratov was supported by ESF Project 2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141.