

Recombination Luminescence in LaPO₄-Eu and LaPO₄-Pr Nanoparticles

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Abstract. *The luminescence properties of LaPO₄-Eu and LaPO₄-Pr nanoparticles with various sizes (8–50 nm) are studied upon the excitation by VUV and X-ray quanta. The dependences of luminescence intensity on nanoparticle size for nanoparticles LaPO₄-Pr and LaPO₄-Eu possessing, respectively, by the electron and hole recombination luminescence at the excitation by quanta of various energies are discussed.*

Key words: luminescence, nanoparticles, luminescence excitation spectra in UV and VUV ranges.

I. INTRODUCTION

Size effect for free excitation luminescence was extensively studied in semiconductor nanoparticles. For example, in semiconductor nanoparticles the quantum confinement leads to the blue shift of the band-gap as well as excitonic absorption peak energy. However, in wide bandgap oxygen-containing nanoparticles, where the exciton size is commensurate with a lattice parameter, the quantum confinement effects are practically absent even for nanoparticle with sizes about 5-10 nm [1-5]. For the luminescence upon the high-energy excitation of wide bandgap insulator nanocrystals, where the luminescent processes are caused by the self-trapped excitons or recombination processes involving the activator ions the size effects can be caused by the commensurability of the mean free path of photoelectrons (holes) and nanoparticle size [1,6,7]. In the paper the dependence of luminescence intensity on the nanoparticle size for nanoparticles LaPO₄-Pr and LaPO₄-Eu possessing, respectively, by the electron and hole recombination luminescence is studied. The dependence of luminescence intensity on the nanoparticle size is not only fundamental but also applied task important for elucidation of possible application of nanoparticles for creation of new nanocomposite materials or even the nanoscintillators for medical use.

II. EXPERIMENTAL

LaPO₄-Eu and LaPO₄-Pr nanoparticles have been synthesized by the template micelle method using the surfactants. The size of nanoparticles was changed in process of high temperature annealing. The nanoparticle size was determined by the X-ray diffraction and TEM. The luminescence measurements were performed at the SUPERLUMI station of HASYLAB at DESY [8].

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III. RESULTS AND DISCUSSION

The emission spectra of LaPO₄-Eu nanoparticles with different sizes are shown in fig. 1, a. The dependence of nanoparticles symmetry on their size has been revealed for LaPO₄-Eu based on the analysis of the structural changes in the luminescence spectra of Eu³⁺-ions and X-ray diffraction data. Nanoparticles with mean size of 8 nm possess hexagonal crystalline symmetry.

Nanoparticles with mean grain size more than 40 nm possess monoclinic symmetry of lattice inherent for LaPO₄-Eu microcrystals (fig. 1, b, c). Observed quantity of Stark's splitting components in nanoparticles of 8 and more than 40 nm size agrees with the hexagonal and monoclinic crystalline symmetry of nanoparticle, respectively.

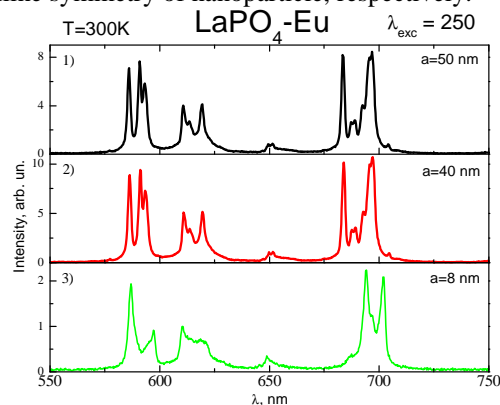


Fig. 1. Luminescence spectra of LaPO₄-Eu³⁺ nanoparticles of various size *a* upon the excitation in CT band (250 nm) at 300 K. Curves: 1 – *a*=50 nm; 2 – *a*=40 nm; 3 – *a*=8 nm.

It is possible to distinguish the next characteristic peculiarities in the excitation spectra of Eu³⁺ in LaPO₄-Eu (Fig. 2): (i) the excitation band connected with charge transfer (CT) from O₂⁻ to Eu³⁺ at E_{CT}~5.0 eV, (ii) the range of optical creation of self-trapped exciton (hν ~8.2 eV), (iii) the range of band to band transitions and range of electronic excitations multiplication (hν > 13 eV). Threshold for electronic excitation multiplication indicates that these processes involve the charge transfer transitions, because E_{th}~E_g+E_{CT}. The 0.24 eV energy shift of CT band to higher energies was observed for small nanoparticles (8 nm) in comparison with microcrystals (Fig. 2). It is most probably that mentioned shift appears due to different lattice symmetry of LaPO₄-Eu microcrystals (for nanoparticles with size more than 40 nm) and nanoparticles of 8 nm size (monoclinic and hexagonal, respectively).

The intensity of the Eu³⁺ ion luminescence generally decreases with decrease of nanoparticles size. It can be explained by greater influence of near surface defects in nanoparticles with smaller sizes. However, the tendencies of

luminescence intensity decrease differ for different energy of excitation quanta. The charge transfer band is least sensitive for the changes of nanoparticle size. The range of direct optical creation of exciton is low sensitive to decrease of nanoparticle size, too. Most sharp decrease of luminescence intensity is observed upon the excitation in the range of band-to-band transitions $E_g < h\nu < (E_g + E_{CT})$. The luminescence intensity upon the excitation in the range of electronic excitation multiplication decreases similarly as upon the excitation in the direct optical creation of exciton. For small nanoparticles (8 nm) the form of excitation band corresponding to electronic excitation multiplication differs from that for nanoparticles of 40 nm and microcrystals. One can suppose that in small $\text{LaPO}_4\text{-Eu}$ nanoparticles the excitation multiplication occurs preferably through the creation of secondary excitations involving the charge transfer transitions.

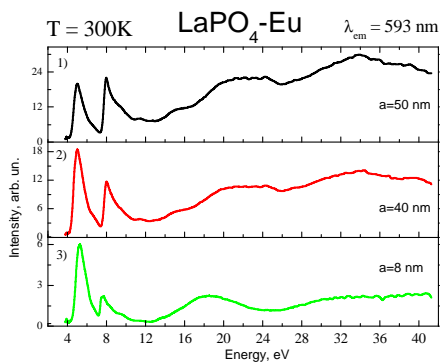


Fig. 2. Luminescence excitation spectra of $\text{LaPO}_4\text{-Eu}^{3+}$ nanoparticles of various size a for Eu^{3+} emission (593 nm) at 300 K. Curves: 1 – $a=50$ nm; 2 – $a=40$ nm; 3 – $a=8$ nm.

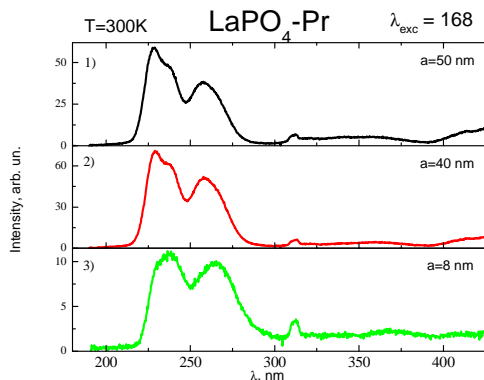


Fig. 3. Luminescence spectra of $\text{LaPO}_4\text{-Pr}^{3+}$ nanoparticles of various size a upon the excitation in $4f\text{-}5d$ absorption band of Pr^{3+} ions (200 nm) at 300 K. Curves: 1 – $a=50$ nm; 2 – $a=40$ nm; 3 – $a=8$ nm.

The $5d\text{-}4f$ radiative transitions in Pr^{3+} ion in the emission spectra of $\text{LaPO}_4\text{-Pr}$ nanoparticles are observed (fig. 3). The luminescence intensity falls with decreasing of nanoparticle size. The $5d\text{-}4f$ luminescence is mainly excited in the range of $4f\text{-}5d$ transitions in Pr^{3+} ions (5.0-7.5 eV) and in the range of the electronic excitation multiplication with the threshold near $2E_g \approx 16.2\text{eV}$ (Fig. 4). For small (8 nm) $\text{LaPO}_4\text{-Pr}$ nanoparticles the praseodymium emission is excited practically only in the range of $4f\text{-}5d$ absorption bands, luminescence intensity is small for excitation with quanta

$h\nu > 2E_g$. The observed regularities in luminescence intensity dependence on nanoparticle size can be explained by surface losses and release of photoelectrons and secondary electrons from nanoparticles due to exceeding of the mean free path or thermalization length of the nanoparticle size.

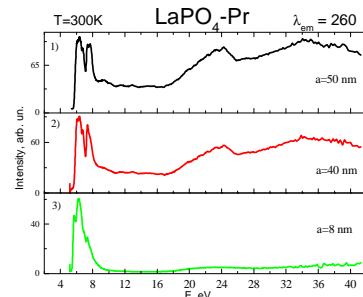


Fig. 4. Luminescence excitation spectra of $\text{LaPO}_4\text{-Pr}^{3+}$ nanoparticles of various size a for $5d\text{-}4f$ emission of Pr^{3+} ions (260 nm) at 300 K. Curves: 1 – $a=50$ nm; 2 – $a=40$ nm; 3 – $a=8$ nm.

IV. CONCLUSIONS

Luminescence properties of $\text{LaPO}_4\text{-Eu}$ and $\text{LaPO}_4\text{-Pr}$ nanoparticles essentially depend on their sizes. This dependence is influenced by the surface defects which lead to nonradiative losses of excitation energy, however, the ratio between thermalization length or mean free path of photoelectrons and the nanoparticle sizes is critical for luminescence intensity. If the thermalization length or mean free path of hot charge carriers exceeds the size nanoparticles the luminescent emission essentially decreases.

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