Intrinsic luminescence of $LaPO_4$ nanoparticles upon UV and VUV excitation

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The size effects for free excitons which are revealed in the form of quantum confinement, interference of coherent excitons, etc. are well studied for the quantum dots in semiconductors. The conditions for quantum confinement effect manifestation for self-trapped excitons with radius commensurable with cell parameters (~10 Å) in wide bandgap particles of nanoscale size (5-10 nm) are not satisfied. In a case of wide bandgap insulator particles the size effects connected with relationship between the free path of band charge carriers and nanoparticles size can considerably influence on self-trapped excitons, which are responsible for fundamental absorption edge and intrinsic luminescence of materials [1].

In our work we present low-temperature (10 K) of self-trapped exciton (STE) luminescent properties of pure $LaPO_4$ nano-particles with different size (8-50 nm) studied under vacuum ultraviolet and ultraviolet synchrotron radiation (3.6 – 20 eV) emitted from DORIS III storage ring at SUPERLUMI station, HASYLAB (DESY, Hamburg).

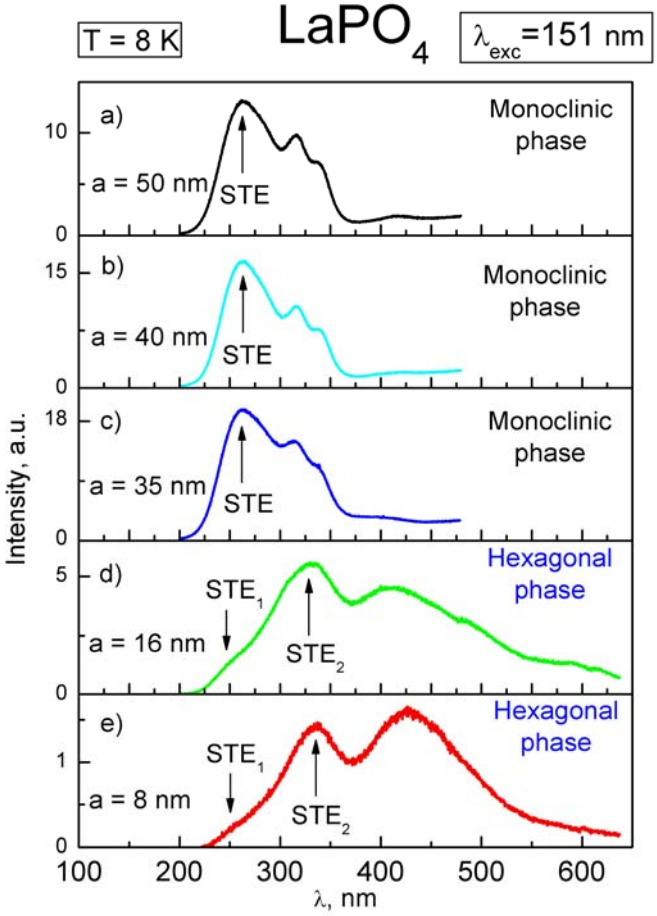

Figure 1: Emission spectra of $LaPO_4$ nanoparticles with different sizes at 8 K.

Emission spectrum of the $LaPO_4$ nanoparticles annealed at 800 ^oC with size of 50 nm possesses the main emission band in the range of 265 nm (Fig. 1). This band is assigned to emission of self-trapped exciton [2]. Besides STE emission in luminescence spectra the bands peaked at 320 and 340 nm were observed. Latter luminescence bands correspond to emission of Ce^{3+} ions, which are present in nanoparticles as uncontrolled impurity. The same structure of emission spectra observed also for $LaPO_4$ nanoparticles with grain size of 35 and 40 nm. As it was obtained from X-ray diffraction measurements the $LaPO_4$ nanoparticles of 35-50 nm size possess the monoclinic symmetry of crystal lattice. The nanoparticles of smaller sizes (8-16 nm) possess the hexagonal symmetry of crystal lattice. The structure of emission spectra for nanoparticles with size of 8-16 nm noticeably differs from that for nanoparticles with grain size of 35-50 nm. For these particles there are two luminescence bands peaked at 260 and 335 nm that one can assign to emission of STE. Besides STE emission the broad emission band in the range of 425 nm appears for $LaPO_4$ nanoparticles of 8-16 nm grain size.

In the luminescence excitation spectra of STE emission for $LaPO_4$ nanoparticles of 35-50 nm size the excitonic absorption band was observed at 8.17 eV (Fig. 2, a-c). Spectral position of this band practically does not depend on the nanoparticles size in the range of (35-50 nm). For nanoparticles with smaller size (16 and 8 nm) possessing the hexagonal structure of crystal lattice the exciton absorption band is observed at lower energies ~ 7.6 eV (Fig. 2, d, e). The luminescence band

peaked at 425 nm appearing in nanoparticles of 8 and 16 nm is excited in the transparence range of $LaPO_4$ host (Fig. 2, e). The nature of this emission is not clear. Because this luminescence band appears in nanoparticles of very small size, one can assume that the emission is caused by surface defects.

The significant dependence of intrinsic luminescence intensity of $LaPO_4$ nanoparticles on their size and on the energy of exciting quanta is observed. Upon the excitation in the range of optical creation of self-trapped excitons the luminescence intensity decreases at the decrease of the nanoparticle size, however this decrease is not so sharp as upon the excitation in the range of recombinational creation of excitons. Practically, the luminescence of self-trapped excitons is not excited by quanta with energies $E_g<E<2E_g$ for nanoparticles of 8-16 nm size; in the same time the self-trapped exciton emission of low intensity upon the excitation in the range of multiplication of electronic excitation onset ($E>2E_g$) is remained yet. The absence of STE emission for small nanoparticles (8-16 nm) at excitation by quanta with energy $E_g<E<2E_g$ can be explained by commensurateness of band charge carriers free path and nanoparticles size. Under this condition the charge carriers (electrons and holes) can achieve the nanoparticle surface and to be trapped by the surface defects. In this case the STE will not be created.

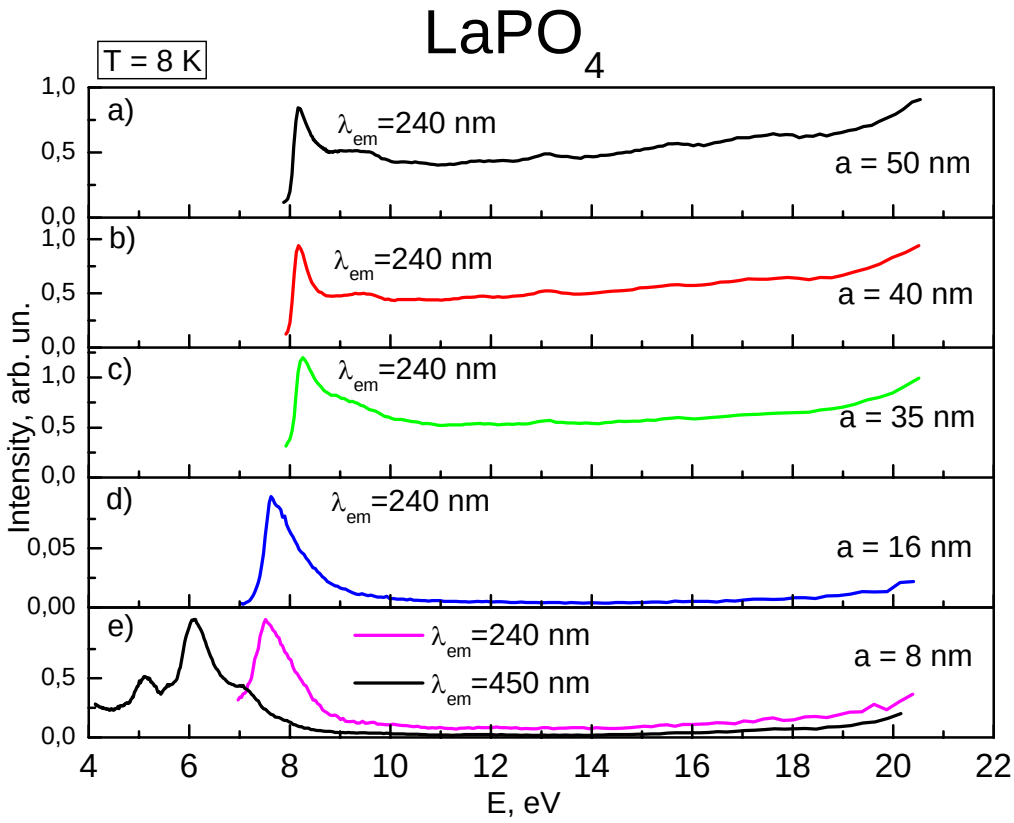

Figure 2: Luminescence excitation spectra of $LaPO_4$ nanoparticles with different sizes at 8 K.

References

[1] V. N. Makhov, Ch. Lushchik, A. Lushchik, M. Kirm, Zhi-Fang Wang, Wei-Ping Zhang, Min Yin, Jing-Tai Zhao. Journal of Luminescence 129 (2009) 1711–1714.

[2] G. Stryganyuk, D.M. Trots, A. Voloshinovskii, T. Shalapska, V. Zakordonskiy, V. Vistovskyy, M. Pidzyrailo and G. Zimmerer. Journal of Luminescence 128 (2008) 355-360.