Luminescence of Defects, Impurity Cr\textsuperscript{3+}-Centers and STE in Nanostructured α-Al\textsubscript{2}O\textsubscript{3} Crystals

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The studies of electronic excitations (EE) and exciton states in nanostructured aluminium oxide crystals are very actual due to their wide practical application [1,2]. The relaxation processes essentially depend on a phase crystalline structure of synthesized nanosamples and they considerably differ from such processes in single macrocrystals [1-4].

The present study was carried out by the means of the low-temperature luminescence VUV and XUV spectroscopy with the time-resolution. The steady-state and time-resolved photoluminescence (PL) spectra, the PL decay kinetics were measured under selective excitation by SR on a SUPERLUMI station. The measurements of PL spectra were made using an ARC Spectra Pro-308i monochromator and an R6358P Hamamatsu photomultiplier. The PL was recorded in two time windows – fast: delay $\delta t_1 = 2.8$ ns, $\Delta t_1 = 8.5$ ns; – slow: $\delta t_2 = 120$ ns, $\Delta t_2 = 50$ ns. The time-integrated and time-resolved PL spectra (2.5–9.0 eV), the PL excitation spectra (in regions of 2L-edge of Al and 1S-edge of O) as well as the PL decay kinetics has been measured at 9 K using SR from the BW3 beamline. The PL spectra were measured by a 0.4 m vacuum monochromator (Seya-Namioka scheme) equipped with microchannel plate-photomultiplier (MCP 1645, Hamamatsu). The parameters of time windows – fast: $\delta t_1 = 0.2$ ns, $\Delta t_1 = 17$ ns; – slow: $\delta t_2 = 54$ ns, $\Delta t_2 = 84$ ns.

The objects of our studies were samples of nanostructured aluminium oxide powders synthesized by method of explosion of a wire, see in detail [5,6]. In addition, the nanopowder was heat treatment for preparation of α-phase Al\textsubscript{2}O\textsubscript{3} (the heating to temperature 1550 °C + subsequent 5 hours annealing – type I nanocrystals and the heating to temperature 1550 °C + subsequent 30 hours annealing – type II nanocrystals, we shall use such designations in text). The type I nanocrystals had the homogeneous size of 90 nm, the type II nanocrystals had the average size in range of 1000 nm. The synthesized nanocrystals were certificated by a methods of the X-ray phase analysis and scan electron microscopy [5,6].

![Figure 1: PL spectra and PL excitation spectra of type I (1, 3-5) and type II (2) nanocrystals α-Al\textsubscript{2}O\textsubscript{3}. $E_{\text{exc}}=10.8$ eV, $T=295$ K. Curve (3) and insert: fragment of PL spectra Cr\textsuperscript{3+} ions recorded using CCD-camera.](image)

The analysis of presented results permit to make following conclusions – resume for nano α-Al\textsubscript{2}O\textsubscript{3} crystals. 1) At differ excitation energy we can observe a PL of defects (310 nm band), Cr\textsuperscript{3+} ions (\textsuperscript{2}E→ \textsuperscript{4}A\textsubscript{2} transition, so named R-line) and low temperature PL of self trapped excitons - STE (7.5 eV). The 310 nm emission band can not correspond to F\textsuperscript{−}-centers in sapphire, we believe that it is a
PL of excitons, localized on defects in type I and type II nanosamples. 2) The R-line can be effectively excited in region of charge transfer band (6.9 eV), in exciton region (9.05 eV) and in photon multiplication region at $E_{\text{exc}}>2E_g$. Bound impurity excitons are very manifestation in type I nanosamples. 3) The increase of nanocrystal size: i) sharply reduces a opportunity of formation of bound (on Cr$^{3+}$- ions) excitons, though the R-line is observed in PL spectrum also still; ii) transformed electron structure of defects, probably, the surface-modification states of F-like defects are observed in nano $\alpha$-Al$_2$O$_3$; iii) reduces the PL decay time and PL yield of STE. 4) The observed size effects can be interpreted as specific spectroscopy manifestations of spatial restriction of EE movement - confinement effect, known in some low size systems. A increase of the nanosize leads to the transformation of electronic structure of defects, as well as to increase of migration losses and occurrence alternate predominitory nonradiation channels of EE (STE) relaxation.

Figure 2: Time-resolved PL excitation spectra for 320 nm emission band: fast (1), slow (2), steady-stay (3) and for 694 nm R-line (steady-stay) – (4,5) in type I (5) and type II (1-4) nano $\alpha$-Al$_2$O$_3$, $T$=9K.

Figure 3: PL decay kinetics in 320 nm emission band in type I (1) and type II (2-4) nano $\alpha$-Al$_2$O$_3$ at $T$=295K (1,2) and 9 K (3,4). $E_{\text{exc}}$= 8.95 (1,2), 9.05 (3) and 10.8 eV (4). Fit of curve (3): $\tau_1=6.5$ ns, $\tau_2=34$ ns.

Figure 4: Time-resolved PL spectra of single crystal (1), type I (2) and type II (3) nanocrystals $\alpha$-Al$_2$O$_3$.

Figure 5: PL decay kinetics in 7.5 eV emission band (STE - emission) of single crystal $\alpha$-Al$_2$O$_3$ (1,2), type I (3,4) and type II (5,6) nanocrystals $\alpha$-Al$_2$O$_3$ at $T$=9 K: $E_{\text{exc}}$= 130 eV (1,3,5) and 525 eV (2,4,6).

References