Alumina is widely used technological material in the form of ceramics or single crystals. The electronic properties of its stable $\alpha$-phase have been thoroughly investigated [1,2]. The metastable polymorphs ($\beta, \gamma, \delta, \Theta$, etc.) known as transition alumina have mainly found theoretical attention. In $\alpha$-$\text{Al}_2\text{O}_3$ all Al ions have octahedral coordination (AlO$_6$), whereas in transition aluminas some of them are tetrahedrally coordinated (AlO$_4$). The number of occupied tetra- or octahedral sites varies for different polymorphs, which leads remarkable differences in their properties. The main goal of our work was to study electronic properties of $\delta$- and $\Theta$-phases of alumina and comparison of properties with $\alpha$-phase. Also effects due to size of particles may influence optical properties of nano-powders.

The plasma processing technique [3] was used to prepare nanopowders from the raw alumina of 99.7 % purity. The obtained alumina powder was in the mixed $\delta$-, $\Theta$-$\text{Al}_2\text{O}_3$ crystallographic phase with spherical particle shape of 75 and 40 nm average size $s$ (specific surface area 20 and 50 m$^2$/g, respectively). Experiments with synchrotron radiation (SR) was performed at the SUPERLUMI station (Strahl I) using time windows technique (length $\Delta t$ and delay $\delta t$). Additional cathodo-luminescence (CL) studies was performed in Tartu using laboratory setup.

As shown in Fig. 1a the electron beam excitation results in several overlapping emission bands with maxima at 5.5, 4.5, 3.3 and 2.2 eV. Selective excitation by 4.1 eV photons reduces a number of bands and the main luminescence maximum is near 3 eV. In time resolved spectra fast nanosecond and considerably slower microsecond components were found at 3.1 and 2.6 eV, respectively. Photoexcitation at 8.27 eV adds luminescence bands in UV region (Fig. 1b and c). There is always present an emission near 1.7 eV with a long decay time, which was assigned to the $R_{\Theta}$ doublet (the $^{2}E \rightarrow ^{4}A_2$ transition of Cr$^{3+}$ d$^3$ configuration) on the basis of high resolution emission spectra.

Fig. 3 shows excitation spectra, where the main feature is a notable excitation onset at $\sim$7.5 eV observed for all emissions being in agreement with earlier results [4]. This onset is assigned to the beginning of intrinsic absorption of transition alumina. Theoretical studies predict also the reduction of energy gap in a row of $\alpha > \kappa > \Theta > \gamma$ alumina from 6.72 to 4.40 eV [5]. It is caused by the formation of additional sub-bands on the top of valence band due to nonbonding oxygen orbitals in oxides. In transition alumina also a downshift of conduction band bottom occurs caused by change of potentials due to shorter Al-O bond distances of Al$^{3+}$ ions in tetrahedral coordination [5].

Two types of self-trapped excitons (STEs) were revealed in $\alpha$-$\text{Al}_2\text{O}_3$ with nanosecond emissions at 7.6 and 3.7 eV [2]. The shrinkage of the energy gap by $\sim$1.8 eV of transition alumina influences also energetic positions of relaxed excited states. UV emission bands are efficiently excited at energies above 7.5 eV, which allows assign those to intrinsic ones. The 5.5 eV band is due to singlet STE emission with ns decay kinetics (not shown, $\tau$= 2.2 ns and 13.3 ns) being an analogue of 7.6 STE emission of $\alpha$-$\text{Al}_2\text{O}_3$. Recent studies under XUV excitation at the BW3 beam-line fully support this assignement. The 4.6 eV emission has considerably longer decay time and can be either due to triplet STEs or of recombination luminescence near defect or impurity centre.

In the transparency region, there is a competition between defect and impurity absorption as the excitation spectra of various centres behave oppositely (Fig. 3a and b). In $\alpha$-$\text{Al}_2\text{O}_3$ [1] presence of F$^-$ and F-centres is well established, emitting at 3.8 and 3.0 eV with the decay times of 2.1 ns and 36 ms, respectively. The 3.1 eV emission of transition alumina has lifetime in few ns range ($\tau$$_2$= 2.7 ns and $\tau$$_3$=12.5 ns), also its excitation spectrum consists of 3 peaks, which is typical for transparency range of defect rich $\alpha$-$\text{Al}_2\text{O}_3$. Therefore, it is assigned to the F$^-$ centres in transition alumina as well.
Figure 1. Left: a - Cathodoluminescence spectrum (1) of nano-alumina (20 m²/g) at 5 K and its VUV-UV part (1') recorded through double prism and vacuum monochromators, respectively. The signal intensities of spectra were adjusted in the overlapping 5.0-5.2 eV region of both monochromators and the curve (1') is increased by a factor of 5 in order to visualize short-wavelength emissions. Emission spectra of the same sample at 8 K excited by 4.1 eV photons of TI (2), fast (3, δt=5.5 ns, Δt=55 ns) and slow components (4, δt=61 ns, Δt=109 ns). The intensity of latter curve (4) is multiplied by 10. b – Emission spectra of nano-alumina (20 m²/g) at 10 K. TI emission excited by 8.27 eV photons (4), TI (5) and slow (δt=85 ns, Δt=77 ns) component (6) excited by 7.09 eV photons. c - Emission spectra of nano-alumina (50 m²/g) at 10 K. TI (7) and fast (δt=1.8 ns, Δt=13.9 ns) component (8) excited by 8.27 eV photons and TI emission excited by 16.5 eV photons (9).

Right: Excitation spectra of nano-alumina (a and b – 20 m²/g, c -50 m²/g ) at 8 K. a –TI 4.43 eV emission (triangles), TI 3.1 eV emission (blue line) and its slow component (circles, δt=61 ns Δt=109 ns), respectively. b – TI 1.75 eV emission (dashed green line), TI 5.5 eV emission (black line) and its slow component (circles, δt=85 ns Δt=77 ns). c-4.43 eV emission (circles), 3.1 eV emission (blue line) and 1.75 eV emission (dashed green line) all recorded in TI mode.

Earlier the 3.2 eV emission has been assigned to the surface F⁺ centres in alumina nanopowders [6]. The 2.6 eV emission with a long decay is tentatively assigned to F-centre luminescence.

Our study did not reveal any significant effects of particle size, which is obviously too large to see any quantum confinement in wide gap insulators with small radius electronic excitations. The main effect observed was the decrease of luminescence intensity because of rising contribution of non-radiative processes on surfaces. The spectral features in the luminescence of 50 m²/g alumina (i.e. in sample with smaller particle size) samples are influenced by inhomogeneous broadening effects. The determined energy gap of δ-, Θ- alumina is 7.6 eV.

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References