Electronic transitions in $\alpha$, $\theta$ and $\gamma$ polymorphs of Ultraporous Monolithic Al$_2$O$_3$

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Ultraporous alumina (UPA) attract considerable interest because of their potential applications in photocatalysis, THz optics, adsorption, etc. They serve to be excellent supporting matrices for active components. In this connection, their electronic structure and optical transitions are of high interest. In this communication we report on first investigation of optical electronic transitions in $\alpha$, $\theta$ and $\gamma$ UPA polymorphs by time- and energy resolved spectroscopy method.

The experiments were performed at the SUPERLUMI station of HASYLAB at synchrotron DESY. Briefly, samples are cooled down to 7K and irradiated by monochromatized ($\Delta \lambda=0.3$ nm) SR under high vacuum ($\sim 10^{-9}$ mbar). The luminescence spectra and decay curves were measured in the UV-visible-nearIR and VUV spectral range. The luminescence excitation spectra were measured in the UV-VUV spectral range in short $\Delta t_1=3$-8 ns and long $\Delta t_2=50$-100 ns with respect to the excitation SR pulse of 130 ps duration. The recorded spectra were corrected for the SR intensity and primary monochromator transmission.

The UPA samples were obtained at room temperature, in humid atmosphere, by oxidation of aluminum plates through a liquid mercury-silver layer [1]. This process directly produces monolithic samples with a high porosity (99 %) and a specific surface area of about 300 m$^2$/g. The microstructure consists of tangled hydrated alumina fibers with a diameter of 5 nm. After thermal treatment at 870°C (4 hours), the crystallization of ultra-porous alumina begins, and $\gamma$-alumina polymorph is first formed with grains size of 7 nm. Above 1100°C, it turns into $\theta$-alumina with the average grain size of 10 nm and the specific area is between 100 and 110 m²/g. At 1200-1250°C, transformation into $\alpha$-alumina occurs, leading to a porous microstructure with a 200-300 nm grain size and specific area of 5-10 m²/g.

The luminescence (L) and luminescence excitation (LE) spectra of the prepared UPA(\(\alpha\)), UPA(\(\theta\)) and UPA(\(\gamma\)) samples are shown in Figure 1. Several L bands in the ultraviolet (UV1, UV2, UV3) and visible (V1) spectral range have been observed, as indicated in the figure. The UV1 and UV2 emissions are short-lived (nanosecond), while V1 and UV3 are long-lived (longer than microsecond). The spectra of several alumina polymorphs were previously discussed. In particular, emission at 7.6 eV and fast component of 3.8 eV emission in the bulk $\alpha$ crystals were assigned to the decay of optically generated excitons [2]. Consequently, the short-wave emissions at 4.6 eV and 5.5 eV in the mixed $\delta$/\(\theta\) nanopowders have been tentatively assigned to triplet and singlet self-trapped excitons (STEs) [3].

Our observations in UPA(\(\alpha\)) sample generally confirms this analysis, providing a better resolution of the emission bands. Indeed, the 3.8 emission in the bulk $\alpha$ crystals splits into two UV2 (5.2 eV) and UV3 (4.1 eV) bands with respectively fast and slow decays. Their LE spectra, shown in Figure 1, are quite different. That of the UV2 band is similar to that of the UV1 band: both show no significant excitation beyond the exciton domain. They can be assigned to localized excitons. The LE spectrum of UV3 band shows the exciton peak similar to that of the UV1 and UV2 bands. However, it has a considerable contribution from both interband excitation above 9.28 eV. It can be therefore assigned to STE produced indirectly, by recombination of free and trapped charges. At excitation below band gap energy, another short-lived broad band with maximum at 3.7 eV appears. Its contribution explains the LE spectrum of the UV3 emission in 5-9 eV region.

The analysis of UPA(\(\theta\)) sample evidences UV1, UV2 and V1 emissions: UV1 is fast and UV3 contains fast and slow components. Similar monoeponential decays of UV1 bands of the $\alpha$ and $\theta$ UPA samples $\tau=18\pm2$ ns indicate their common nature. Consequently, the UV1 band can be assigned to a decay of localized excitons and its excitation maximum at 8.16 eV may have the excitonic nature. Significant contributions of both exciton and interband excitations may indicate STEs formed by direct excitation and by free-trapped charges recombination mechanism. Under this assumption, the bandgap energy of UPA(\(\theta\)) is estimates to 8.5±0.1 eV. Similar to the UPA(\(\alpha\))
sample, only the slow component of the UV3 band shows excitonic features of UV1 band. The fast component is excited in the 7.5-5 eV region.

![Diagram showing luminescence and luminescence excitation spectra of α, θ, and γ polymorphs of UPA (Al₂O₃).](image)

Figure 1: Luminescence (left) and luminescence excitation (right) spectra of α, θ and γ polymorphs of UPA (Al₂O₃).

Only two UV3 and V1 bands show up in UPA(γ) sample L spectra. Similar to UPA(θ), the UV3 emission contains fast and slow components, which LE spectrum shows an inflection at 6.85 eV. In agreement with the above-discussed polymorphs, this feature can be assigned to the bandgap energy. Significant contributions of the interband excitations above 6.85 eV may indicate STEs formed in this polymorph preferentially by free-trapped charges recombination mechanism.

The fundamental absorption onsets of the UPA samples are in a general agreement with the theoretical predictions by Lee et al. [4] of the band gap narrowing in the order of α > θ > γ.

The V1 bands in all UPA samples are rather similar in spectral position, shape and lifetime (long). These bands have not been reported in previous studies [2,3]. They can be tentatively assigned to anion vacancies.

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References