INTRINSIC EXCITONS IN $12CaO \cdot 7Al_2O_3$

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Functionality of $12CaO \cdot 7Al_2O_3$ (C12A7) is highly variable due to its unusual nanocaged crystal structure. Its unit cell consists of 12 positively charged (+4 per unit cell) interconnected cages with an inner free space of ~0.4 nm diameter. Various negative ions (O^{2-}, O^-, F^-, Cl^-, H^-, OH^- etc.) can be incorporated (up to $2.3\times10^{21}/cm^3$) inside these cages to maintain charge neutrality of the lattice (Hayashi et al., 2007). Even electrons can be encaged playing a role of anions and in fully electron loaded C12A7 its conductivity is metallic. Unusual crystal structure causes extraordinary electronic properties of C12A7 as well. According to the theory (Sushko et al., 2007) there are s-like unoccupied states inside empty cages. These states form low energy conduction band, the cage conduction band (CCB) located within the framework band gap of C12A7. This narrow CCB is positioned ~5.5 eV above the top the valence band. In our previous work (Feldbach et al., 2009) the framework energy gap value was determined by luminescence spectroscopy methods. The value $E_g \approx 6.8$ eV is in good agreement with the formation energy of intrinsic excitons (~6.6 eV) based on the Urbach tail study (Hayashi et al., 2007).

Like in other wide gap materials on can expect pronounced intrinsic excitonic effects, which are not so well investigated in C12A7. The main aim of our present work was to analyze possible evidences of excitons revealed in low temperature time-resolved luminescence under VUV at SUPERLUMI station (HASYLAB, DESY) and electron beam excitation in Tartu. Several possible mechanisms can contribute to formation of excitonic states in C12A7 due to the unoccupied CCB states and the existence of localized electrons inside the cages. In the case of electron loaded C12A7, exciton-like states can be formed from the encaged electrons and holes localized on the O^{2-} ions constituting the wall of that occupied cage. The UV luminescence band peaked at ~5 eV is assigned to radiative decay of those localized excitons, because the onset of its excitation spectra is at ~E_g, which is necessary condition for creation of holes in the valence band. This luminescence typical for singlet excitons was present in all our investigated samples with the encaged electrons. Its decay is well described with the sum of two exponentials decays of ns range, which is tentatively assigned to the excitons with different hole components localised on two non-equivalent O^{2-} sites. However, most of the cages in C12A7 (at least 8 of the unit cell 12) are always empty independently of encaged species. One can expect excitonic excitations formed in such cages. Charge transfer excitation between neighboring empty cages can result in formation of an intra-cage triplet exciton proposed by Sushko et al, 2006. The luminescence band peaked at ~2.1 eV, which has no temperature dependence (up to 300 K) with a long decay time (τ>200 ns) is the most probable candidate for the evidence of these excitons. Its excitation band found below the onset of band-to-band transitions (framework band gap) supports our hypothesis.

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