Dependence of luminescence excitation spectra in the VUV region on the size of \( \text{Y}_2\text{O}_3\)-Yb nanoparticles

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Using time resolved excitation spectroscopy we studied the dependence of charge-transfer (CT) and exciton emissions on the dimension of \( \text{Y}_2\text{O}_3\)-Yb nanoparticles. Luminescence and scintillation properties at the nanoscale are a very interesting subject in terms of potential nanoscintillator application. While the optical response of nanostructures under low energy excitation is currently studied, the scintillation response under high-energy excitation above the band gap energy was barely the object of investigation.

Nanoparticles have been elaborated by the polyol mediated synthesis method using nitrate precursors. The initially obtained powder of \( \text{Y}_2\text{O}_3\)-Yb is composed of small nanoparticles (<3 nm) [1]. The ytterbium concentration in nanoparticles is about 2%. The powder was subsequently heat treated at different temperatures, from 400°C to 1000°C. The heat treatment implies a growth of the nanoparticles. Those thermal treatments are well below the melting temperature of the pure sesquioxides \( \text{Y}_2\text{O}_3 \) and \( \text{Yb}_2\text{O}_3 \). The nanoparticles grow respectively to 13 nm, 21 nm, 28 nm, 43 nm, 52 nm and 61 nm for annealing temperatures of 500°C, 600°C, 700°C, 800°C, 900°C and 1000°C. For each temperature, XRD measurements of particle size were performed.

Figure 1a presents time-resolved luminescence excitation spectra of 21 nm particles. Excitation spectra in the region \( E \leq E_g \) consist of two principal peaks. The spectrum of slow component is in good correlation with excitation spectrum of intrinsic luminescence in \( \text{Y}_2\text{O}_3 \) [2]. The peak at the energy 6.2 eV is placed in the low-energy part of the excitation spectrum of UV band in non-doped crystals and can be associated with creation of exciton. In agreement with [2], we can conclude that the low energy excitation band at 5.5 eV in time integrated and in fast spectra corresponds to the CT absorption band.

In nanoparticles the ratio of intensities of these two peaks differs from that for \( \text{Y}_2\text{O}_3\)-Yb single crystal, and changes with the particle size (see fig. 1b). The variation is not monotonous: for smallest particles (13nm) the CT band is more intense than the excitonic peak (the ratio \( I_{\text{CT}}/I_{\text{EXC}} \) is about 1.3). With the increase of the particle size (21 nm) the CT band decreases relatively to the excitonic one. For 52 nm NP this ratio falls down to 0.5. However, for the single crystal the CT band increases again, \( I_{\text{CT}}/I_{\text{EXC}} = 2 \). We suppose the same concentration of Ytterbium in all samples and the Yb sites in \( \text{Y}_2\text{O}_3 \) matrix are the same as in the single crystal. Therefore, the nature of variation of excitation spectra with particle dimensions should be related to the size effect. The quantum size effects can be neglected in ionic materials for NPs with dimensions over 10 nm. For particles of intermediate size (less than 100 nm) the principal effects are related to energy transfers and light scattering.

In luminescent nanoparticles the decrease of luminescence efficiency with particle size can be often related to the increase of energy losses by energy transfers to the surface states. In \( \text{Y}_2\text{O}_3\)-Yb the spectra of CTL and exciton emission overlap. The transfer to the surface states efficiency must be comparable for both excited states. Moreover, with increase of particle size from 13 to 60 nm the
average distance between surface and exciton created by VUV photons remains the same, since the absorption coefficient for exciton band is about $10^6$ cm$^{-1}$. On the opposite, the average distance from CTL state and surface increases due to the relatively weak CTL state absorption coefficient. The discussed phenomenon in Y$_2$O$_3$-Yb nanoparticles is the opposite to the effect induced by the surface losses in nanoparticles of intermediate sizes.

Another possible explanation is connected with the variation of light scattering with particle dimensions. The scattering is definitely strong for the investigated samples (they are white colour with strong diffusion reflection). The scattering results in the increase of the diffuse reflection and therefore the decrease of the fraction of excitation light absorbed by the media. This effect is much stronger in the case of low absorption coefficient (i.e. for the CT band) than in the case of high absorption coefficient (i.e. for the exciton band and fundamental absorption range). The scattering is directly determined by the ratio of the particle diameter to the wavelength $\lambda$. The peak of the scattering from the media consisted of particles with diameter $d$ correspond to $d \sim \lambda/2\pi$. Therefore, the peak of scattering of 5 eV photons corresponds to particle diameters about 50 nm. The scattering strongly decreases for smaller particles (the Rayleigh law results in $d^3$ dependence for $d<<\lambda/2\pi$) and for particles with macroscopic sizes (and therefore for single crystal sample).

At higher energy, the excitation efficiency strongly decreases; it is 10 times less at 10 eV. Luminescence intensity starts to increase again above 14 eV. This energy (E>2Eg) can be connected with the threshold of multiplication of electronic excitations in Y$_2$O$_3$. Efficiency at 17 eV of excitonic luminescence in undoped crystal is close of 80% of excitation at exciton absorption band. All nanoparticles demonstrate the good conversion efficiency for energetic photons. For NP 52 nm the intensity under excitation by 17 eV photons is higher than the intensity at low energy excitation.

References