Charge transfer luminescence of Yb$^{3+}$ and intrinsic luminescence in sesquioxides Lu$_2$O$_3$, Y$_2$O$_3$, Sc$_2$O$_3$ and Yb$_2$O$_3$

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The charge-transfer luminescence (CTL) of Yb-doped crystals is attractive for scintillator applications [1]. The characteristics of the CTL in Yb-doped sesquioxides were studied recently [2]. Here we report on the mechanism of energy transfer from the matrices to the CTL centers as well as on the effects of intrinsic luminescence on the CTL in Yb-doped sesquioxides.

Single crystals of pure and Yb-doped Lu$_2$O$_3$, Y$_2$O$_3$, Sc$_2$O$_3$ and Yb$_2$O$_3$ were grown in the Institute of Laser Physics (University of Hamburg) by the Heat-Exchange-Method derived from the Bridgman technique. Luminescence spectra, excitation of the luminescence and decay kinetics were measured at the SUPERLUMI station.

Luminescence spectra of the CTL in Yb-doped sesquioxides (fig. 1) consist of two broad bands in the range 1.5 - 4.5 eV. The characteristics of this luminescence: bandwidth about 1 eV, energy separation between the bands about 1.3 eV and nanosecond decay kinetics (from few nanoseconds in Yb$_2$O$_3$ and Sc$_2$O$_3$-Yb to tens of nanoseconds in Y$_2$O$_3$-Yb and Lu$_2$O$_3$-Yb at 8 K) are typical for the charge transfer transitions in Yb-containing compounds. The low-energy luminescence band at 1.5-3 eV is assigned to the transitions from the charge transfer state (CTS) to the $2F_{5/2}$ state of Yb$^{3+}$ ions and the high-energy luminescence band at 3-4.5 eV is assigned to the transitions from the CTS to the $2F_{7/2}$ state of Yb$^{3+}$ ions.

At the same time intrinsic luminescence of undoped crystals is located in the region of high-energy CTL band 2.5 – 4.5 eV (fig.2). In spite of similar bixbyite-type crystal structure of Lu$_2$O$_3$, Y$_2$O$_3$ and Sc$_2$O$_3$ the origin of these luminescence bands is different due to different electronic structure: self-shrunk exciton in Y$_2$O$_3$, tunnel luminescence in Sc$_2$O$_3$ [3] and recombination of electrons and self-trapped holes in Lu$_2$O$_3$ [4]. While in case of Y$_2$O$_3$ the intrinsic luminescence decay time is longer than microseconds and thus it can be easily discriminated from the CTL, in case of Lu$_2$O$_3$ and Sc$_2$O$_3$ nanosecond components are observed both in the intrinsic luminescence and in the CTL, the excitation spectra of both types of luminescence are presented in fig. 3,4.
Two regions can be separated in the excitation spectra of the CTL in Yb-doped sesquioxides: the region from ~5 eV to ~6 eV is the region of direct CT absorption followed by the region of fundamental absorption at higher photon energies (fig.3). The fundamental absorption edge of Yb$_2$O$_3$ can be estimated from the onset of the CTL slow component (originating from delayed recombination of separated electrons and holes) as ~5.8 eV. In Y$_2$O$_3$ and Lu$_2$O$_3$ it can be estimated from the position of the first peak in the reflectivity spectra: 6.0 eV in Y$_2$O$_3$ and 5.8 eV in Lu$_2$O$_3$. In Sc$_2$O$_3$ no reflectivity peak was detected, the fundamental absorption edge can be estimated from the onset of intrinsic luminescence excitation (fig. 4) as being not less than 6.2 eV. The CTL excitation spectra of Y$_2$O$_3$-Yb, Sc$_2$O$_3$-Yb and Yb$_2$O$_3$ are similar in the range 9-27 eV. Low CTL yield in the range 9-14 eV demonstrates that this is luminescence of excitonic type and separated electrons and holes have a low probability of the energy transfer from the matrix to the CTS.

![Figure 3: Excitation spectra of the charge transfer luminescence (3.6 eV) in Lu$_2$O$_3$-2%Yb (1), Y$_2$O$_3$-3%Yb (2), Sc$_2$O$_3$-0.7%Yb (3) and Yb$_2$O$_3$ (4) at 8 K.](image)

Different behavior of the excitation spectra of intrinsic luminescence in pure oxides Y$_2$O$_3$ and Sc$_2$O$_3$ and excitation spectra of 3.6 eV luminescence in Yb-doped Y$_2$O$_3$ and Sc$_2$O$_3$ confirms that in doped crystals it is really CTL which we observe at the excitation in the fundamental absorption region, not the intrinsic luminescence. In the excitation spectrum of the CTL of Y$_2$O$_3$-Yb the minimum at 6 eV corresponds to the maximum in the excitation spectrum of the intrinsic luminescence in the undoped crystal, indicating a competition between two types of luminescence in Y$_2$O$_3$-Yb. In Sc$_2$O$_3$-Yb the increase of the intensity in the CTL excitation spectrum at 6.2 eV reproduces the increase in the excitation spectrum of the intrinsic luminescence of undoped Sc$_2$O$_3$. In contrast to Y$_2$O$_3$-Yb and Sc$_2$O$_3$-Yb the excitation spectrum of the CTL in Lu$_2$O$_3$-Yb in the fundamental absorption range is different from the CTL excitation spectrum of Yb$_2$O$_3$ but is similar to that of intrinsic luminescence in pure Lu$_2$O$_3$. Since intrinsic luminescence band centered at 3.5 eV in pure Lu$_2$O$_3$ overlaps with the CTL both luminescence types can be detected in the excitation spectrum of Lu$_2$O$_3$-Yb. At the same time since in Lu$_2$O$_3$ intrinsic luminescence band with the maximum at 4.8 eV (this band was observed in Yb-doped crystals under excitation in the fundamental absorption range as well) overlaps with the CT absorption the energy transfer from the intrinsic luminescence to the CTL is to be considered as well.

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References