The Effect of Growing Conditions and Thermal Treatment on Luminescent Properties of CaWO₄ Crystals

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Calcium tungstate crystals are one of the most widely used phosphors due to their excellent luminescent properties, in particular, strong visible luminescence, high light yield as well as high resistance to external environmental influences. Moreover, CaWO₄ is perspective material for lasers, acousto-optic components or scintillators [1, 2]. However, spectroscopic and physical characteristics of CaWO₄ can vary significantly depending on a difference in the quality of samples. It should be noted also, the presence of a strong afterglow emission component quite often undermines CaWO₄ use.

Single crystals were grown by the Czochralski technique from raw materials having purities of 99.99%. The excitation and luminescence spectra of different kind of CaWO₄ single crystals were investigated at room temperature.

The CaWO₄ single crystals exhibit a strong luminescence emission in the wavelength range of 350-650 nm with X-ray and UV excitations. The position of this band maximum varies from 450 to 520 nm for crystals of different origin. Accordingly, the luminescence intensity and band position of phosphors depend strongly on the starting materials of which are single crystals grown.

The maxima of elementary emission bands, as well as half-widths, were determined. It was established also, that the type of crystals, as well as the excitation wavelength, affect the relative intensity of elementary emission bands.

Measured emission spectra at high energy excitations, in particular, more than 4.9 eV, are mainly attributed to the charge-transfer transitions within the $[WO_4]^{2-}$ anion complex and is interpreted as an emission of self-trapped excitons. The relative intensity of the long-wavelength luminescence band, attributed to the emission of structural defect of the lattice, for example, oxygen-deficient WO₃ complex, in CaWO₄ crystals, increases at low energy excitations (4.2-4.4 eV). The nature of the additional luminescence band located between two the above-mentioned is under discussion.

The mechanism of afterglow emission in $CaWO_4$ crystals also is investigated by means of X-ray luminescence and thermally stimulated luminescence (TSL). It was established, that decreasing of the afterglow intensity is accompanied by a lowering of the deep traps concentration.

The influence of annealing in an oxygen atmosphere on luminescent properties of CaWO₄, including the relative intensity of elementary emission bands as well as afterglow emission, was also investigated.

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