Spectroscopy of the Yb^{3+} Ions in the $PbWO_4$ Crystals

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The lead tungstate crystals ($PbWO_4$) are successfully applied for many years as scintillator materials and host matrices for Raman lasers. The RE doping of these crystals is a very important for the both applications. For lasers, the RE dopants are used as activator ions. As for the $PbWO_4$ scintillators, adding of the RE impurities is used for decreasing of lead and oxygen vacancies concentrations, because such vacancies are the most probable defects in the $PbWO_4$ crystals grown by Czochralsky method. Therefore, study of luminescence mechanisms and excitation energy transfer between the RE impurities and matrix is very important for the $PbWO_4$ crystals. Luminescence properties of the Yb^{3+} ions in the $PbWO_4$ matrix were reported previously only episodically and poorly [1-3]. In the present work, we have carried out an investigation of luminescence properties of the impurity Yb^{3+} ions in the $PbWO_4$ matrix and search of mutual correlations in behaviour of matrix emission and impurity emission.

The $PbWO_4:Yb^{3+}$ crystals were grown by the Czochralski method using the "Crystal-617" installation. The blend was synthesized from lead, tungsten and ytterbium oxides. Concentration of the impurity in the blend was $5x10^{-2}$ wt %. Our analysis showed that impurity concentrations in the grown samples were reduced. The rectangular 5x10x10 mm bricks used for the investigation were cut from the central part of the crystal bulk.

Luminescence emission of the Yb^{3+} ions was observed in the 970 – 1040 nm spectral range. At room temperature, emission is presented by weakly structured band. Experiments carried out at 10 K with fine spectral slits of spectrometers reveal that this band consists of 16 narrow spectral lines. The observed spectrum of linear emission is caused by *f-f* $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions in the Yb^{3+} ions. The $^2F_{7/2}$ level in crystal field can be split on 8 Stark components maximally. Observed 16 spectral components can be easily divided on two groups by dependence of their relative intensities on excitation wave length. The group of more intensive lines (975, 978, 996.5, 998, 999.5, 1001, 1023 and 1032 nm) was assigned to the first type of emission. These lines are intensive in the spectra obtained at 300 – 340 nm excitations. Their intensities significantly fall down at excitations with $\lambda_{ex} < 300$ nm, whereas intensity of rest lines assigned to the second type of emission does not depend on excitation wavelength. The relative contribution of the Yb^{3+} emission to the matrix emission is also strongly depended on excitation wavelength. The distinctive raise of the first type of lines intensity correlates with the shift of maximum position of the wide band visible emission from 445 – 455 nm at $\lambda_{ex} < 300$ nm to 510 nm at $\lambda_{ex} = 309$ nm.

Structure of the Yb^{3+} emission centres is discussed. The observed significant differences between spectral properties of two types of centres formed by the Yb^{3+} ions in the $PbWO_4$ crystal lattice are explained by different ways of the impurity ions incorporation on Pb and W sites for the first and second types of centres, respectively. These two types of centres have different symmetry of the Yb^{3+} ions (C_s and D_2) and crystal field strength due to differences between ionic radii of lead, tungsten and ytterbium ions. Correlations in behaviour of the Yb^{3+} emission and matrix emission are analyzed.

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