

# The Influence of Chromium Impurity on the Spectral Characteristics of ZnWO<sub>4</sub> Crystals

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**Abstract**—The absorption, excitation, and emission spectra under photo- and X-ray excitation of ZnWO, ZnWO<sub>4</sub>:Cr<sup>3+</sup> zinc tungstate crystals have been investigated. The charge trapping and the radiative thermally stimulated recombination processes in ZnWO<sub>4</sub> involve six trapping states at 107, 129, 152, 170 K and 200, 235 K. The activation energies of traps which are responsible for appearance of TSL in the region 80-300 K were estimated.

**Index Terms**—78.55.Hx; 78.60.Kn; 78.70.Ens—**Keywords**—photo- and X-ray luminescence; thermostimulated luminescence; ZnWO<sub>4</sub>

## I. INTRODUCTION

Zinc tungstate (space group *P2/c*) with a width of the band gap of  $E_g \approx 4.6$  eV has a monoclinic crystalline structure of wolframite-type [1]. High energy resolution, low level of radioactive background and good signal resolution by particle types make ZnWO<sub>4</sub> suitable for searching for double beta decay of isotopes of zinc and tungsten, study of alpha decays of tungsten isotopes, as well as for use as a dark matter particle detector [2-4]. Crystals of zinc tungstate have a smaller light yield than the most effective crystals on the basis of alkali metal iodides, but they are not hygroscopic, easy to preparation, can be obtained as nanosized crystals. The main disadvantage of these materials is the strong dependence of the quality of crystals on the presence of impurities and growing conditions [1, 5]. The slow decay of scintillation due to the presence of structural and impurity defects limits the using of the ZnWO<sub>4</sub> scintillator in cases where large registration speeds are required [5].

The development of science and technique in different areas associated with the using the luminescent materials, led to an increase works on the synthesis and study of crystalline

phosphors doped with the impurities of iron group ions [6-8]. On other hand, the crystals doped with ions of transition metal are widely used as effective materials for solid state lasers. In spite of many studies devoted to research of the ZnWO<sub>4</sub> crystals, activated by the ions of transitional metals, by the Cr ions in particular, nature of recombination luminescence and mechanisms of thermoactivation processes in these materials have not been studied sufficiently.

Basing on the literature data, the results of the spectral-luminescence characteristics of ZnWO<sub>4</sub> crystals and ZnWO<sub>4</sub>:Cr<sup>3+</sup> samples after their long-term storage under laboratory conditions in an air atmosphere are analyzed in the paper.

## II. EXPERIMENTAL

For the present investigation ZnWO<sub>4</sub> single crystals were grown from platinum crucibles by the Czochralski method [1]. The impurities were entered as Cr<sub>2</sub>O<sub>3</sub> oxide. The content of Cr impurity was ~0.5 mol. %. Samples in a thickness of 0.5-1.0 mm were obtained by cleaving the crystal in a (100) plane. Chromium 3d<sup>3</sup> ions replace two-valent cations Me<sup>2+</sup> in a regular lattice and occupy a distorted octahedron formed by oxygen ions in ZnWO<sub>4</sub> crystals. Since the crystals doped with Cr<sup>3+</sup> ions were grown without the introduction of an ion compensator, the problem of compensating for excessive charge could be solved by the creation of one vacancy Zn<sup>2+</sup> ( $V_{Zn}$ ) on two Cr<sup>3+</sup> ions. Local charge compensation is carried out by the vacancy of zinc ( $V_{Zn}$ ) with a localized on it one hole corresponding to the formation of a neutral associate.

Spectroscopic investigation of samples in the case of X-ray excitation was carried out in helium cryostat with the using a setup based on the MDR-12 diffraction monochromator. Scanning and recording of the X-ray luminescence spectra

were carried out with a computerized system. Emission in the spectral region 350-850 nm was measured in single photon mode using FEU-51 photomultiplier. X-ray excitation was provided by a URS-55A X-ray generator and Mo-target BSV-2 X-ray tube ( $U=45$  kV,  $I=10$  mA) through the beryllium window of the cryostat. The curves of thermostimulated luminescence (TSL) were recorded in the integral mode under linear heating of samples at a rate  $\sim 0.07$  K/s. The temperature was set with the accuracy of 0.1 K in the range of 80-500 K. Investigation of optical-luminescence characteristics of crystals in the case of optical excitation at 300 K was carried out on a spectrofluorimeter CM 2203. The device provided a possibility to measure the spectra of excitation and luminescence in the spectral region of 200-820 nm.

### III. RESULTS AND DISCUSSION

Absorption spectra of  $\text{ZnWO}_4$  tungstate are characterized by a sharp increase of the absorption coefficient in the region of the fundamental absorption edge [1]. The absorption spectra in the visible region of the activated with  $\text{Cr}^{3+}$  crystals are represented by wide bands at  $\sim 510$  and  $715$  nm, due to the  ${}^4A_2 \rightarrow {}^4T_1$  and  ${}^4A_2 \rightarrow {}^4T_2$  transitions in  $\text{Cr}^{3+}$  ions, respectively. Activator absorption band with maximum at 340-345 nm which associated with the  ${}^4A_2 \rightarrow {}^4T_1$  ( ${}^4P$ ) transitions is observed in the spectral range near matrix absorption edge. Emission spectrum of  $\text{ZnWO}_4$  at 90 K is represented by a non-elementary band with a maximum near 480 nm (Fig. 1).

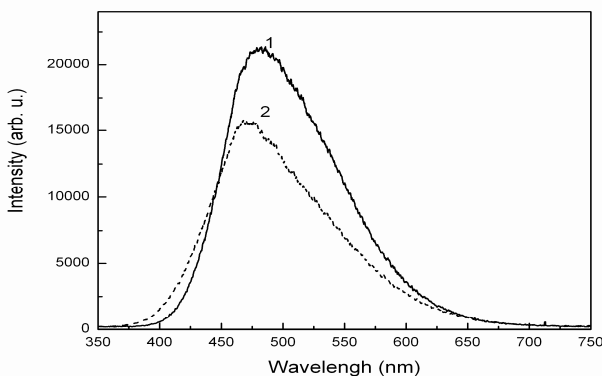


Figure 1. XRL spectra of  $\text{ZnWO}_4$  crystals at 90 (1) and 300 K (2).

At this temperature the  $\text{ZnWO}_4$  is characterized by an inertial rise of steady-state X-ray luminescence (XRL). The previous X-ray irradiation of the sample for a further 90 minutes leads to a slight shift of maximum of the emission spectrum to short-wave range. With an increasing temperature up to 300 K, the luminescence intensity decreases by 30 %, there is a decrease in the half-width of the spectrum and a shift of its maximum to 470 nm. The spectra of XRL are characterized by a superposition of several partially overlapping basic elementary bands with maxima of about 440 nm (2.84 eV), 480 nm (2.59 eV) and a relatively weak band of 600 nm (2.04 eV). In the case of optical excitation of  $\text{ZnWO}_4$ , a 460 nm wideband luminescence, which is a superposition of several bands, is also observed [9]. The shift of the X-ray and photoluminescence spectra relative to each other is attributed

to the change in the ratio of the relative contribution of the elementary emission bands by reducing the intensity of the band 480 nm in the case of high-energy excitation. The 480 nm intrinsic luminescence of  $\text{ZnWO}_4$  is excited in a main band with maximum of about 270 nm and on a bend at 310 nm at 300 K. The excitation spectrum of the matrix emission in  $\text{ZnWO}_4:\text{Cr}$  is characterized by a maximum in the region of the long-wave edge of the own absorption.

Doping  $\text{ZnWO}_4$  with  $\text{Cr}^{3+}$  ions leads to a decrease of the matrix luminescence intensity by approximately an order of magnitude, while weakly affects the spectral composition of the matrix emission. A significant decrease of matrix luminescence intensity in the doped crystals can be explained by the absorption of this emission by  $\text{Cr}^{3+}$  ions and the redistribution of the energy of radiative transitions in favor of activating centers luminescence with a maximum of about 900-1000 nm (transition  ${}^4T_2 \rightarrow {}^4A_2$ ) [9]. Rise of the activator content is accompanied by an increase of the luminescence intensity of  $\text{ZnWO}_4:\text{Cr}^{3+}$  in long wave range with the decay time  $\sim 10^{-5}$  s [1].

From the analysis of the obtained experimental results and the literature data, it follows that the long-term storage of samples does not affect the emission processes in zinc tungstate. A typical intrinsic luminescence band with a maximum of 480 nm, which is dominant in the XRL spectrum, is caused by the radiative decay of self-trapped excitons of oxyanion complex  $\text{WO}_6^-$ . Under excitation by optical illumination with a wavelength of 310 nm, optical transitions that are associated with the transfer of charge from oxygen to the conduction band on the tungsten states of the  $\text{ZnWO}_4$  crystals are predominantly occurring, which leads to the creation the self-trapped excitons on these complexes. In the case of excitation in the fundamental absorption band by photons with a wavelength of about 270 nm, the luminescence occurs with previous binding the electron and hole in exciton. Observed similar features in the spectral characteristics of luminescence of the investigated  $\text{ZnWO}_4$  crystals and  $\text{CdWO}_4$  isostructural crystals [10] make it possible to assume that elementary Gaussian bands with a maximum of about 440 and 600 nm are related to radiation in oxyanion groups located near defective complexes containing cationic and anion vacancies, respectively.

The stage of transfer of separated electrons and holes to the luminescence centers depends on the presence of traps in the forbidden gap and significantly affects the scintillation mechanism. Studies have shown that the intensity of the peaks and the shape of the TSL curves are quite sensitive to the conditions for the preparation of  $\text{ZnWO}_4$  crystals and the heating rate of the samples. Characteristic is that this material stores light sums mainly on the deep levels responsible for the peaks of TSL above 180 K. The presence of traps, which manifests itself at high-temperature peaks of TSL, is due to the slow components of the  $\text{ZnWO}_4$  glow at 300 K [5].

The TSL curve after X-ray excitation of  $\text{ZnWO}_4$  crystal at a temperature of 90 K for a 5 minutes and a further heating rate  $\beta$  of sample  $\sim 0.07$  K is characterized by a superposition of weak peaks at 107, 129, 152, 170 K and peaks 200, 235 K

with a higher intensity (Fig. 2). Increasing the time of the previous X-ray excitation of the sample to 30 minutes leads to an increase of TSL intensity approximately in 3.5 times, while not affecting the position of the peaks.

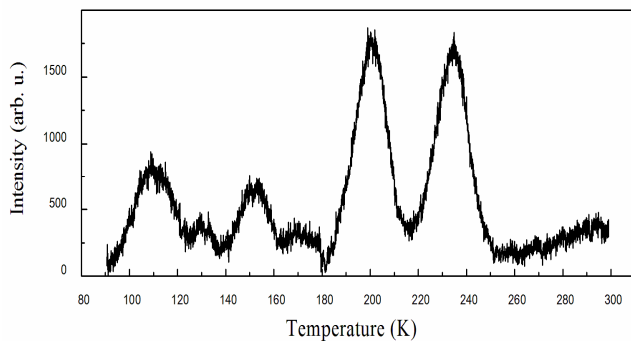


Figure 2. TSL curve of the crystal  $\text{ZnWO}_4$  after X-ray excitation at 90 K.

In [1] it was assumed that the lowest-temperature TSL peaks of the  $\text{ZnWO}_4$  crystals, on the one hand, and the highest-temperature peaks on the other hand, have opposite signs of the relaxation mechanism. It is established that the peaks of thermoluminescence in the 80-200 K range in  $\text{ZnWO}_4$  have a spectral composition similar to the spectral composition of the steady-state luminescence. The highest-temperature peaks (above 200 K) exhibit long-wavelength thermoluminescence with a maximum at 620 nm. The identity of the spectral composition of the low-temperature TSL peaks and the XRL spectra obviously indicates that the steady-state XRL is the result of the recombination of holes with electrons at electron trap levels. The concentration of capture centers responsible for high-temperature peaks is definitely regulated by the presence of defects (mainly vacancies) in the cation sublattice [1].

All four low-temperature weakly intense peaks are partially overlapped. Therefore, an approximate formula was used to estimate the depth of the levels responsible for these peaks  $E(\text{eV}) = T_{\text{max}}(\text{K})/540$  [11]. According to this formula it is determined that peaks at 107, 129, 152 and 170 K correspond to activation energies  $E_a \approx 0.20, 0.24, 0.28$  and  $0.31$  eV, respectively. The analysis of the shape of TSL curve showed that for the dominant peaks at 200 and 235 K, the true ratio  $T_h - T_m < T_m - T_l$ , where  $T_l, T_h$  is the temperature corresponding to half the peak height at the low temperature and high-temperature branches;  $T_m$  – position of the maximum of the peak on the TSL curve. Assuming that these peaks are elementary and  $\Delta = T_h - T_l$  and  $\delta = T_h - T_m$ , determined parameters of asymmetry of peaks (form factor)  $\mu_g = \delta/\Delta$ . For both peaks values are obtained  $\mu_g \approx 0.46$  and  $0.41$ , which corresponds to the kinetics of the first order [12] and the process of release of the stored light takes place in monomolecular kinetics.

To estimate the depth of traps for a linear case of kinetics at  $A_p > A_c$  used the proposed by Ch.B. Lushchik [13] expression:  $E = k_B T_m^2 / \delta$  ( $k_B$  – Boltzmann constant;  $A_c$  – probability of capture,  $A_p$  – probability of recombination). The thermo activating parameters of the dominant peaks were also calculated by the formula [12]:  $E = 2,52 k_B T_m^2 / \Delta - 2 k_B T_m$ . The

values of the thermal depth of the traps that are related to the dominant peaks obtained by different methods were averaged. It was established that the peaks of TSL at 200 and 235 K correspond to activation energies  $E \approx 0.48$  and  $0.68$  eV [1]. The doping of  $\text{ZnWO}_4$  crystal by chromium impurity leads to a significant reducing of thermoluminescence. A weak peak at 107 K is recorded on the TSL curve of the  $\text{ZnWO}_4:\text{Cr}^{3+}$  crystal. Due to its ability to change the valence state, the chromium impurity is an effective center for capturing the nonequilibrium charge carriers [14]. The recombination of a free electron with centers of  $\text{Cr}^{4+}$ , or a hole localized on a zinc vacancy, converts  $\text{Cr}^{3+}$  into an excited state  $(\text{Cr}^{3+})^*$ . The transition  $(\text{Cr}^{3+})^*$  to the ground state is accompanied by the activator emission in the long-wavelength region of the spectrum with a maximum of about 900-1000 nm, which is not recorded when measuring the TSL curves.

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