Influence of oxygen on luminescent properties of ZnWO$_4$ crystals surface

L A Lisitsyna

$^1$Tomsk state university of Architecture and Building 634003, Tomsk, Solyanaya sq., 2 Building 2, Russia

E-mail: lisitsyna@mail.ru

Abstract. The results of studies of emission properties of oxygen-containing ZnWO$_4$ crystals are presented. Oxygen is incorporated into single crystals in two ways: annealing of crystals at 900 C in an oxygen atmosphere and implantation of high energy (28 MeV) oxygen ions. The observed variation of the photoluminescence intensity and excitation spectrum of emission at 2.6 eV are interpreted as the occurrence of a concentration gradient of emission centers in the crystal bulk under heating of crystals and the dependence of the photons mean penetration depth in a crystal on their energy. In order to gain better insight into the nature of the phenomenon, time-resolved luminescence measurements were carried out.

1. Introduction

The effect of the state of the surface and surface associated physical phenomena on inherent spectral-kinetic parameters of a phosphor luminescence is one of the less studied issues. It requires further investigation and more detailed analysis. The actuality of the research is determined by application of scintillators, both large-volume and nano-sized ones, in a variety of environments and temperatures, and by the need to maintain stable parameters during long-lasting operation of scintillators.

To understand the role of the surface we investigate stationary luminescence excitation spectra of the crystals subjected to different types of treatment and with nanosecond time-resolution the luminescence excited by ionizing radiation in ZnWO$_4$ crystals.

2. The tasted samples and the experimental method

Three types of sources were used for the luminescence excitation: (i) an electron beam pulse accelerator with the electron energy of 250 keV, pulse duration of 10 ns and a radiation dose absorbed by the crystal within the action of the electron pulse equal to $5.10^1$ Gy; (ii) pulsed Nd-YAG laser irradiation with photon energy of 4.66 eV, pulse duration of 10 ns, an energy per pulse of 40 mJ; (iii) xenon steady state lamp with a radiation energy of 3–6.2 eV.

The studied ZnWO$_4$ single crystals were grown by the Czochralski technique at the Institute for Scintillation Materials NAS Ukraine (Kharkov).

Under investigation were the following crystals: i) crystals freshly cleaved from a crystal block; ii) the crystals stored in oxygen atmosphere at 900 C for 50 hours; iii) crystals implanted with the oxygen ions of 28 MeV. The concentration of the implanted oxygen ions was $10^{18}$ ion/cm$^3$.

The spectral-kinetic characteristics of the luminescence were studied in the region of 4–1.5 eV after the different delay times after the end of the excitation nanosecond pulse in the time interval of $10^{-8}$–$10^{-1}$ s. The spectra were not recalculated with account of PMT sensitivity.
3. Results

The spectral composition of the time-resolved luminescence of ZnWO₄ crystals under excitation both with 4.66 eV photons and 250 keV electrons is the same. The emission spectrum of the short-lived decay component is an asymmetric band at 3.1 eV with FWHM equal to 0.5 eV and the decay time constant (τ₁) equal to 10 ns. The emission spectrum of the long-lived decay component is a band at 2.6 eV (Figure 1) with a multi-exponential character of the emission decay. The best fit to the experimental data at 300 K was obtained using three exponentials with the decay time constants of 200 ns, 3 and 25 µs. The obtained spectral-kinetic parameters of the long-lived luminescence coincide with those published for ZnWO₄ crystals in [1-4]. The ratio of the intensities of the emission bands at 2.6 (J₂) and 3.1 eV (J₁) in the photoluminescence (PL) spectra of freshly cleaved ZnWO₄ crystals is more than 1 (J₂/J₁>>1); the ratio of the decay time constants of the emission at these bands τ₂/τ₁≈10³ (where τ₁=10 ns, τ₂=25 µs (the greatest value of the time decay constants at 2.6 eV emission band at 300 K); so the inequality J₂τ₂>J₁τ₁ is satisfied, where J₂ and J₁ are the light yield at 2.6 and 3.1 eV, respectively.

Figure 2 shows the excitation spectrum of the emission band at 2.6 eV for freshly cleaved ZnWO₄ crystals. The excitation spectrum reaches the maximum value at photon energy 3.9 eV and has a substantially constant value in the range 3.9–6.2 eV. (At 6.2 eV, this value is lower than that at 3.9 eV only by 10% in our crystals). According to [2,4–6], the emission intensity at 2.6 eV does not depend on photon energy of 4–7 eV at all, and it is equal to its maximum value at photon energy of 4 eV.

![Absorption spectrum](image1.png)

**Figure 1.** Absorption spectrum (1), photoluminescence spectra of ZnWO₄ crystal (2,3) measured with 10 (2) and 400 ns (3) at 300 K after the action of laser pulse (spectra are normalized).

![Excitation spectra](image2.png)

**Figure 2.** Excitation spectra of emission band at 2.6 eV at 300 K for different ZnWO₄ crystals: freshly cleaved sample (1), oxygen implanted with fluence of 10¹⁵ ion/cm² (2), heated in oxygen atmosphere at 900 C for 50 hours (3).
Implantation of oxygen ions in ZnWO₄ crystals with the fluence of 10¹⁵ ion/cm² changes neither the emission spectrum, nor the excitation spectrum for emission at 2.6 eV (figure 2). There is no change in relative intensities of emission bands at 3.1 and 2.6 eV as well.

Heating of crystals in oxygen atmosphere at 900 C for 50 hours causes the following changes in the spectra luminescence of these crystals.

- Intensity of the emission band at 2.6 eV under 6.2 eV photon energy excitation becomes ~ 80% lower than that under 3.9 eV (figure 2).
- The ratio of the intensities of the emission bands at 2.6 (J₂) and 3.1 eV (J₁): after heating of the crystal changes and the light yields in both bands becomes comparable, i.e., J₁τ₁≈J₂τ₂, whereas, before heating of the crystal J₂τ₂ / J₁τ₁>10⁴. (The duration of the luminescence decay in both emission bands does not depend on the heating).

The heating of crystals does not affect the ratio between the intensities of the emission bands in spectra of photoluminescence (PL) in contrast to the spectra of cathodoluminescence (CL) the hearted crystals. As an example, in the PL spectrum of the heated crystal, the ratio J₂/J₁ is 0.05, whereas, in the CL spectrum of the same crystal, the ratio J₂/J₁ is 5, and it is equal to that in the crystal before heating.

4. Discussion

Decrease of the luminescence at 2.6 eV in annealed crystals under excitation with UV energy photons could result from the following processes: (i) radiationless processes on the surface, (according to [7], it is caused by killer centers created on the crystal surface); (ii) destruction of the luminescence centers responsible for emission at 2.6 eV; (iii) reabsorption of excitation energy by the luminescence centers responsible for emission at 3.1 eV formed during heat treatment.

We propose the following model of the processes. The main statements of the model are set out below.

1) We suggest the presence of two types of emission centers (EC) in ZnWO₄ crystals: ECₖ and ECₜ responsible for the emission at 2.6 eV and at 3.1 eV, respectively. ECₖ are homogeneously distributed within the bulk of the crystal. The mean value of their concentration is high and not less than ~10¹⁷ cm⁻³ is due to the impossibility of maintaining stoichiometry of the melt during crystal growth [8–11] ECₜ are localized on the thin sample surface layer. Their concentration depends on the temperature and duration of crystal storage in air. The minimal number of ECₜ is found on the surface of freshly cleaved crystals, as evidenced by the low intensity of the band at 3.1 eV in these crystals.

2) During heating of crystals in oxygen, the creation of an additional number of ECₖ due to the destruction (transformation) of ECₜ occurs. The concentrations of ECₜ and ECₖ inside the crystal at distance x from the surface are determined by~exp(-x²/L²) and by~(1-exp(-x²/L²)), respectively. (L is the characteristic diffusion length). Heat treatment leads to the depletion of ECₖ in the surface layer, i.e., ECₖ distribution in the crystal becomes non-uniform.

3) To excite luminescence, the crystal is subjected to a photon flux. The photon flux N is equal to 10¹⁳ cm⁻³s⁻¹ and is the same for different values of the photon energy in range of 3–6 eV.

Inhomogeneous distribution in the crystal of the centers ECₖ leads to the satisfaction of inequalities Nₖ>>N and Nₖ≤N in the crystal bulk and in the heated crystal, respectively.

4) The luminescence at 2.6 eV belongs to ECₖ and its intensity is determined by the number of ECₖ in an emission state (Nₖ*). Nₖ* value depends on the relation between Nₖ and N. Obviously, if Nₖ≤N (in the surface layer), Nₖ*~Nₖ. If Nₖ>>N (in the crystal bulk), Nₖ*~N.

5) According to the Buger-Lambert-Beer law, the number of the absorbed photons in a layer of thickness x is given by exp(-kx), where k is an absorption coefficient. The dependence k=f(hv) in the region of 4–7 eV for the ZnWO₄ crystal is published in [12], hence the mean penetration depth (k⁻¹) of photons in a crystal can be calculated as a function of the photon energy. According to our
estimations, if the photon energy decreases from 7 to 4.5 eV, k⁻¹ varies by one order of magnitude (from 10 to 100 nm).

6) The photons with a penetration depth k⁻¹>L preferentially excite the LC in the bulk of the crystal in which Nb>N. The photons with a penetration depth k⁻¹≤L excite the LC in the thin surface layer of crystal in which Nb≤N.

Then, taking into account paragraph (4) of this model, in crystal heated in oxygen, the value of EC₅* depends on two parameters: (i) the distance from the surface of the crystal; (ii) the energy of the photons exciting the emission (i.e., the depth of the photon penetration in the crystals).

Hence, the value of the photon energy, at which the intensity of the luminescence at 2.6 eV decreases, can be used to estimate the depth of the disturbed surface layer in which Nb<N. According to our estimates, the depth of the disturbed surface layer is equal to 80 nm in crystals heated in oxygen atmosphere at 900 C for 50 hours.

7) In the process of oxygen implantation, no additional EC₅ is created on the crystal surface, and as a result, no concentration gradient of EC₅ is observed. The ratio Nb>N is fulfilled in all regions of the crystal, and the intensity of the emission at 2.6 eV does not depend on the photon energy.

Since the implantation of oxygen ions does not result in suppression of the photoluminescence at 2.6 eV, it is obvious that this type of treatment does not cause depletion of oxygen luminescence centers.

There is no doubt that oxygen implantation has an effect on crystal surface, however, it does not lead to creation of the luminescence centers responsible for the band at 3.1 eV. We assume that implantation does cause modification of the oxygen present in the EC₅ composition as it occurs during heating of crystal.

8) Photons with the energy <4 eV, for which the depth of penetration into the crystal k⁻¹>L, as well as the electrons with a penetration depth equal to 0.2 mm (250 keV), excite the emission in the bulk of the crystal, and the effect of the surface state is not so high. As a result, there is no effect of crystal heating on the efficiency of the luminescence excitation at 2.6 eV in the range of photon energy of 3.6–4 eV.

Within the frame of the given model, the coincidence of the excitation spectrum at 2.6 eV in ZnWO₄ macrocrystal heated in oxygen atmosphere at 900 C with that in ZnWO₄ nanocrystal, synthesized in air at 1114 K [13], indicates that in both cases the crystal surface formed at high temperature suppresses the photoluminescence at 2.6 eV.

5. Conclusions
The comparative analysis of the luminescence spectra excited by radiation with different depth of penetration into a crystal revealed the presence of spatial distribution of defects in the material bulk.

A detailed analysis of the time-resolved characteristics of the crystals allows us to suggest the existence of a spatially inhomogeneous structure of the original material imperfection. We suggest two types of LC in ZnWO₄ crystals. One of them, located in the crystal bulk, is responsible for the emission at 2.6 eV. The crystal surface is enriched with LC responsible for the emission at 3.1 eV.

The ratio between the two types of LC changes in favor of the surface LC during heating in oxygen atmosphere or in air, or during crystal storing in air at 300 K. The dependence of the depth of probe radiation penetration into the crystal on radiation energy make the ratio between the intensities of the emission bands of the surface and bulk centers depend on radiation energy. In excitation of the ZnWO₄ crystal bulk not only by high-energy electrons, as shown in this paper, and, apparently, in excitation by X-ray and γ-rays, the state of the surface does not affect the efficiency of the excitation band at 2.6 eV. An extrinsic luminescence band (3.1 eV) at the surface has an insignificant effect on the luminescence spectrum of ZnWO₄ crystal only if the radiation penetrates a significant distance deep in the crystal from its surface.

The observed effect can be used to estimate the energy for heavy particles of low energies.

The value of the threshold photon energy, at which the luminescence intensity at 2.6 eV
decreases in the excitation spectrum, was used to estimate the depth of the disturbed surface layer. For ZnWO$_4$ heated at 900°C in oxygen, this value was found to be equal to 80 nm.

The absence of the dependence of the luminescence intensity on the energy of excitation exceeding the threshold (>4 eV) indicates that the concentration of LC$_b$ in the surface layer does not differ from the average value in the crystal volume.

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