X-ray and photo-excited luminescence of ZnWO$_4$ nanoparticles with different size and morphology

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X-ray and photoluminescence of ZnWO$_4$ nanocrystals with controlled size and morphology: grains with diameter of 10–20 nm; rods with diameter of 10–20 nm and length of 200–250 nm produced by microwave hydrothermal method were studied. Red luminescence with $\lambda_{max} = 700$ nm was found in the samples. The intensity of the red luminescence increases with decreasing of the ZnWO$_4$ nanoparticles size due to increase of concentration of oxygen vacancies and creation of distorted WO$_6$ centers. It was shown that reduction in the X-ray luminescence intensity with decrease of the ZnWO$_4$ nanoparticles size is due to creation of the distorted WO$_6$ centers which are the nonradiative relaxation channel competing with the self-trapped excitons.

Keywords: nanocrystals, ZnWO$_4$, oxygen vacancies, luminescence, scintillator.


Рентген- и фотолюминесценция наночастиц ZnWO$_4$ различных размеров и морфологий. I.A.Тупіця, П.О.Максимчук, Г.Г.Якубовська, Ю.В.Малюкін, В.С.Зверева, О.М.Вовк.

Досліджено рентген- та фотолюминесценцію нанокристалів ZnWO$_4$ з контролюваними розмірами та морфологією: зерна діаметром 10–20 нм; стержні діаметром 10–20 нм і довжиною 200–250 нм, отримані гідротермально-мікрохвильовим методом. У дослідженнях зразків виявлено червону люмінесценцію з $\lambda_{max} = 700$ нм, інтенсивність якої зростає зі зменшенням розміру наночастиц ZnWO$_4$, що обумовлено збільшенням концентрації вакансії кисню і створенням спотворених WO$_6$ центрів. Показано, що зменшення інтенсивності рентгенолюминесценції при зменшенні розміру наночастиц ZnWO$_4$ пов’язано з конкуруючим з автотоксикаційним екситоном безвміштовним каналом релаксації — спотвореними WO$_6$ центрами.
1. Introduction

Zinc tungstate single crystals are known as scintillators for tomography, dosimetric and spectrometric systems used for radiation monitoring, digital radiography, as well as for registration of the more nuclear events [1–3]. Scintillation materials based on ZnWO₄ attract special attention because its parameters are close to such of cadmium tungstate, however, they have low level of radioactivity and are non-toxic on its own [2].

Preparation of nanoscale scintillators based on divalent metal tungstate is actual problem [4–7]. It was developed due to prospective use of inorganic scintillators with a large effective atomic number in medicine and biology for photodynamic therapy [8, 9]. A recent approach relies on use of the scintillating nanoparticles that upon exposure to ionizing radiation, such as X-rays, emit luminescence in the visible region, which, in turn, activates a conjugated photosensitizer through the Forster resonance energy transfer (FRET) [10–15]. X-ray inducible photodynamic therapy has practically no limitation in the penetration depth in tissues. Another advanced application of the nanoscintillators which stimulates its studies is the development of X-ray fluorescence imaging [16–18]. For this purpose, besides increasing of the penetration depth, the known effect of selective accumulation of the nanoparticles in tumor cells is used.

A number of papers relating to the scintillation properties of particles of submicron and nanoscale size in comparison with the bulk crystals describe changes of the material properties due to size reduction [19–21]. This effect is attributed to a change in defects of the crystal structure [19]. The method of modeling of recombinational luminescence intensity dependence on the nanoparticle size is proposed on the basis of assumption that contribution to the recombinational luminescence gives only those charge carriers which in a result of thermalization did not reach a near-surface layer of the nanoparticles [21].

It was shown that X-ray luminescence intensity decreases with decrease of ZnWO₄ nanoparticles size [22,23]. For understanding of nature of this effect the luminescent properties of ZnWO₄ nanoparticles of different size and morphology before and after annealing in oxygen atmosphere have been investigated in this paper.

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2. Experimental

We used the following starting materials: Na₂WO₄⋅2H₂O, Zn(NO₃)₂⋅6H₂O (impurity composition is shown in Table 1), NH₃⋅H₂O of analytical grade purity (98 %).

Synthesis of nanoparticles was carried out in two stages. Initially, amorphous ZnWO₄ was prepared by co-precipitation of 25 ml 0.1 M aqueous solutions of Zn(NO₃)₂ and Na₂WO₄ at the room temperature with vigorous stirring. pH of the solutions was adjusted by adding dilute aqueous 30 % NH₃⋅H₂O solutions. The synthesis was carried out by microwave hydrothermal method on microwave installation MARS (GEM Corporation Matthews, USA) at temperature of 120, 200°C and frequency of 2.45 GHz for 30 min. Upon completion of the synthesis the white precipitate was filtered, washed with distilled water and dried at 70°C in air for 3 h.

Annealing of the nanocrystals was carried out in air at temperature of 400°C for 12 h. This temperature was selected because increasing of grain size was observed at the temperatures higher than 500°C [24].

X-ray phase analysis of the samples was characterized by X-ray powder diffraction (XRD) on Siemens D 500 powder diffractometer (radiation CuKα, nickel filter, Bragg-Brentano geometry).

Morphology of the nanocrystals was investigated by transmission electron microscopy using EM-125 (SELMA, Ukraine) microscope. Electron accelerating voltage was 125 kV, the survey was carried out in the bright field mode, and the image was recorded by CCD matrix.

Luminescence spectra of the nanocrystals were recorded by means of automatic spectrofluorimeter based on the lattice mono-
chromator MDR-23. Photomultiplier Hamamatsu R9110 operated in the photon counting mode was used for luminescence spectra registration. The 3-rd and the 4-th radiation harmonics of YAG: Nd laser ($\lambda_{ex} = 266$ nm and 355 nm) were used as the photoluminescence excitation sources. X-ray generator REYS ($U_{k} = 25$ kV, $i_{k} = 0.37$ μA) was used as an X-ray excitation source.

3. Results and discussion

Structure of obtained ZnWO$_4$ powders was monoclinic (wolframite). TEM images are shown in Fig. 1. We obtained ZnWO$_4$ with grains size of 10–20 nm (further called the “grains”) synthesized under pH – 9.5, $T$ = 120°C conditions. Rods of 10–20 nm in diameter and length of 200–250 nm, referred to as the “rods”, were prepared at pH – 9.5 and $T$ = 200°C.

The luminescence spectra of investigated powders under X-ray excitation at the room temperature are broad asymmetric bands with a maximum at 495–500 nm (Fig. 2). This glow is typical for the bulk ZnWO$_4$ crystals. It is connected with radiative relaxation of excitation on oxygen complex WO$_6^{5-}$ with electron transfer from 5$d$ W on 2$p$ O, traditionally described as a relaxation of the self-trapped exciton [25–27]. Luminescence of the “grains” is insignificant (Fig. 2, cr. 1), while the “rods” have intense glow, practically unchanged after annealing in air (Fig. 2, cr. 3 and 4). The intensity of the “grains” luminescence after annealing in air is greatly increased (Fig. 2, cr. 2).

The measurements of the ZnWO$_4$ nanoparticles photoluminescence spectra (after annealing) under excitation with $\lambda_{ex} = 266$ nm correspond to band with $\lambda_{max} = 470$ nm for the “grains” and “rods”, due to relaxation of the self-trapped exciton, the same as for X-ray excitation (Fig. 3). Under the “rods” excitation at $\lambda_{ex} = 355$ nm in addition to the basic glow at $\lambda_{max} = 470$ nm the broad band luminescence at $\lambda_{max} = 700$ nm of the same intensity was observed (Fig. 3, a). For the “grains” the contribution of red band with $\lambda_{max} = 700$ nm is much greater under the excitation at $\lambda_{ex} = 355$ nm (Fig. 3, b). The both “grains” and “rods” red luminescence band intensity at the room temperature is low, but the glow becomes brighter by almost 2 orders of magnitude if the temperature is lowered to 80 K.

Investigation of effect of annealing of the “grains” in oxygen atmosphere by the red luminescence showed that after the annealing in air the intensity of luminescence...
band of $\lambda_{\text{max}} - 700$ nm decreased by a factor of 2 (Fig. 4).

Reducing of the baseband X-ray intensity ($\lambda_{\text{max}} - 495$ nm) as the size of the nanoparticles decrease (at the same time the intensity of the red luminescence band with $\lambda_{\text{max}} - 700$ nm increases) caused by increasing luminescence centers concentration competing with the glow of the self-trapped excitons. The luminescence of impurities as observed for the bulk crystals ZnWO$_4$ Mo [28] can not occur for our samples because investigated samples have low content of the impurities, in particular Mo less than 1 ppm.

The results allow us to conclude that the red luminescence with $\lambda_{\text{max}} - 700$ nm is more intense for ZnWO$_4$ "grains" and it is associated with oxygen vacancies. This is consistent with the known data for other nanoparticles of inorganic oxide compounds: as nanoparticles size decrease (due to the larger surface deposit) the concentration of the oxygen vacancies increases. In particular, fluorescent techniques show that reduction of CeO$_2$ nanocrystals size (from 75 to 20 nm) leads to increase by 1.5 times the band luminescence of Ce$^{3+}$ stabilized by the oxygen vacancies, whereas CeO$_2$:Eu$^{3+}$ down-sizing leads to symmetry reduction of Eu$^{3+}$ [29]. Also for these nanocrystals extremely high concentrations of the oxygen vacancies and hence Ce$^{3+}$ ions were determined by EPR — 44% for 3 nm size nanoparticles and 17% for 30 nm [30, 31].

WO$_3$ monophase samples were investigated by G.Blasse [32]. The crystalline structure of WO$_3$ relates to perovskite-like compounds containing octahedra with a central ion with $d^0$ configuration. Their luminescence is described by the wide band with $\lambda_{\text{max}} - 700$ nm and its intensity is considerably reduced at the higher temperatures. Similar spectral data were obtained for luminescence complex [WO$_{10}$O$_{32}$]$^{4+}$ [33]. Luminescence of these compounds attributed to transitions with charge transfer in WO$_6$ octahedra, the structural parameters of which (the distance W—O, angles) differ from those of ZnWO$_4$.

In ZnWO$_4$ nanocrystals due to high concentration of the oxygen vacancies, which increases with decreasing the particle size, the WO$_6$-octahedra with a distorted structure close to the structure of WO$_3$ octahedra can form. Annealing in the oxygen atmosphere leads to healing the oxygen vacancies.
decreasing of the lattice distortion and reducing the red emission intensity. The luminescence of such distorted \( \text{WO}_6 \)-octahedra can be described as luminescence of centres with a low probability of emission. Under photoexcitation with energy corresponding to excitation of the luminescence centre, we provide the situation of the most favorable excitation and observe the most intensive emission at the low temperatures. Probability of the radiative relaxation decreases with increasing the temperature due to increasing of the electron-phonon interaction. Under the X-ray excitation the red luminescence was not observed even in the sample with a high concentration of the oxygen vacancies. In this case the distorted \( \text{WO}_6 \) centers appear as a competing nonradiative relaxation channel and luminescence intensity of the main bands decreases.

4. Conclusions

\( \text{ZnWO}_4 \) nanocrystals with controlled size and morphology were obtained by microwave hydrothermal method: grains with diameter of 1.0–20 nm; rods with diameter of 10–20 nm and a length of 200–250 nm.

The luminescence with \( \lambda_{\text{max}} \sim 700 \) nm, the intensity of which increases with decreasing of the \( \text{ZnWO}_4 \) nanoparticles size due to increase of oxygen vacancies and creation of distorted \( \text{WO}_6 \) centers was observed.

It was shown that the decrease of the X-ray luminescence intensity with the \( \text{ZnWO}_4 \) nanoparticle size decreasing is due to the non-radiative relaxation channel — distorted \( \text{WO}_6 \) centres which are competing with the self-trapped excitons.

References

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