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$ZnWO_4$ luminescent films obtained by hydrothermal method

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$ZnWO_4$ films of 10–20 μm thickness can be produced by hydrothermal synthesis method without additional subsequent treatment. The data obtained show that films possess wolframite structure and demonstrate luminescent properties which are similar to bulk $ZnWO_4$.

Пленки $ZnWO_4$ толщиной 10–20 мкм могут быть получены методом гидротермального синтеза без дополнительной последующей обработки. Полученные данные показывают, что пленки имеют структуру вольфрамита и демонстрируют люминесцентные свойства, аналогичные объемному $ZnWO_4$.

1. Introduction

$ZnWO_4$ is considered as an attractive material for different applications due to its optical and chemical properties. For instance, high chemical stability and high X-ray absorption coefficient together with short decay time and low afterglow level make $ZnWO_4$ promising X-ray and γ-ray detecting material [1–4]. Other potential applications of $ZnWO_4$ are laser host [5], acoustic fibers [6], photocatalysis [7, 8]. $ZnWO_4$ is widely used in form of single crystals produced by Czochralski method from a melt. In order to extend application area many efforts are made to obtain and study $ZnWO_4$ in nano-scale and film forms. $ZnWO_4$ films can be prepared by different methods: sol-gel [9, 10], ion beam sputtering [11], spray pyrolysis [12], RF sputtering of WO_3 and ZnO mixture [13]. In this work, $ZnWO_4$ films were obtained by hydrothermal method. There are a few works dealing with $ZnWO_4$ produced by this method but the aim of such synthesis was to obtain nano-scale objects [7, 14–16]. The structure and luminescence properties of $ZnWO_4$ films with thickness up to 20 μm deposited by hydrothermal method are discussed in this paper.

2. Experimental

The amorphous $ZnWO_4$ was obtained by dissolving of 0.1 M aqueous solutions of $Zn(NO_3)_2$ and Na_2WO_4 in 50 ml distilled water at room temperature with constant stirring during 30 min. All initial chemicals ($Na_2WO_4 \cdot 2H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$) of analytical grade were used without further purification. The pH of the aqueous solution was 6.2. The measurements of pH were done using Extended Range Waterproof pH HI 991001. The white precursor obtained was collected and then centrifuged and rinsed out with distilled water several times for concentration and ion admixtures removal. After such treatments resulting white pre-

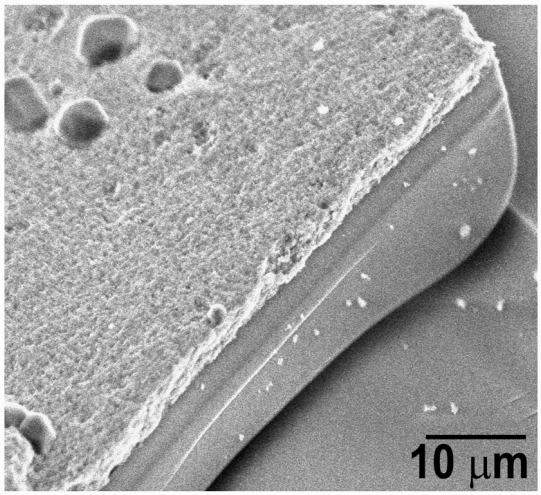

Fig. 1. SEM image of cross-section of $ZnWO_4$ film produced by hydrothermal synthesis on glass substrate.

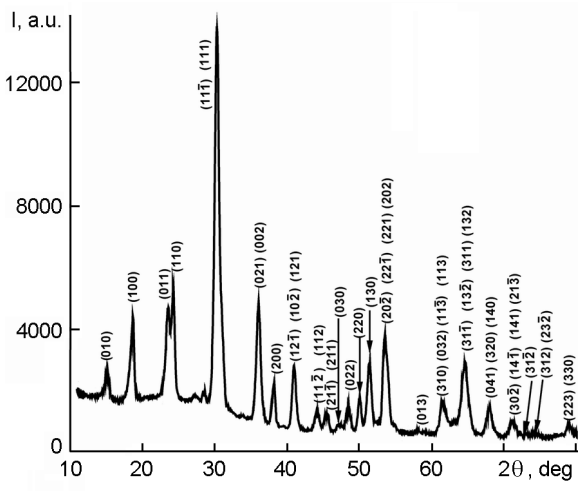

Fig. 2. X-ray diffraction pattern of $ZnWO_4$ film on glass substrate. Miller indices of diffraction planes are denoted.

cursor suspension was transferred into 25 ml quartz test tube. The chemically cleaned glass substrate was vertically installed without contact with suspension inside quartz test tube. Then this tube was placed in custom-made stainless-steel autoclave. The tightly closed autoclave was heated to 200°C and kept at this temperature during 24 h without shaking or stirring. Thereafter autoclave was allowed to naturally cool down to room temperature. Films formed on both sides of substrate were rinsed out with distilled water and dried at 100°C during 2 h for further characterization. Thickness of the obtained films was from 10 up to 20 μm.

The samples morphology was studied with a JSM-6390 LV scanning electron microscope.

Crystalline structure of the films was examined by X-ray diffraction using general purpose X-ray diffractometer at Cu Kα radiation, equipped with graphite monochromator in the primary beam, and in a symmetric θ–2θ mode.

Photoluminescence spectra were recorded using a FLS 920 fluorescence spectrometer (Edinburgh Instruments) with the steady-state Xe900 450W xenon lamp as a UV excitation source. Radioluminescence was studied under X-ray excitation (Cu-anode, 40 μA, 40 kV).

3. Results and discussion

The films obtained by such method are opaque with white color. As one can see in Fig. 1 film is composed of two layers. The

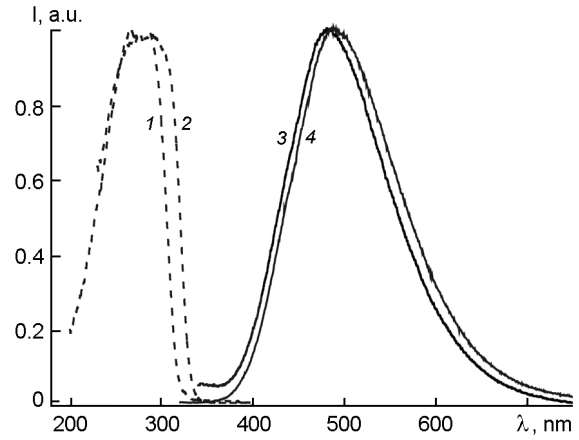

Fig. 3. Excitation spectra of 490 nm emission: (*1*) — $ZnWO_4$ film; (*2*) — bulk $ZnWO_4$. Emission spectra of $ZnWO_4$ film (*3*) and bulk $ZnWO_4$ (*4*) excited by 300 nm.

thick and visually compact layer formed on substrate is covered by thin porous layer.

X-ray diffraction data show that hydrothermal method leads to formation of films which consist of $ZnWO_4$ crystalline phase (Fig. 2). Three unlabeled reflections in X-ray diffraction pattern of $ZnWO_4$ film (Fig. 2) belong to uncertain phase. The structure of $ZnWO_4$ can be illustrated schematically as chains formed of either edge-sharing ZnO_6 or edge-sharing WO_6 octahedrons, which are parallel to *c*-axis [17]. Such distorted WO_6 octahedral complex consisting of W ion surrounded by six oxygen atoms plays an important role in the luminescence properties of $ZnWO_4$ [18–21]. So the presence of such wolframite structure in the produced films has to result in intrinsic

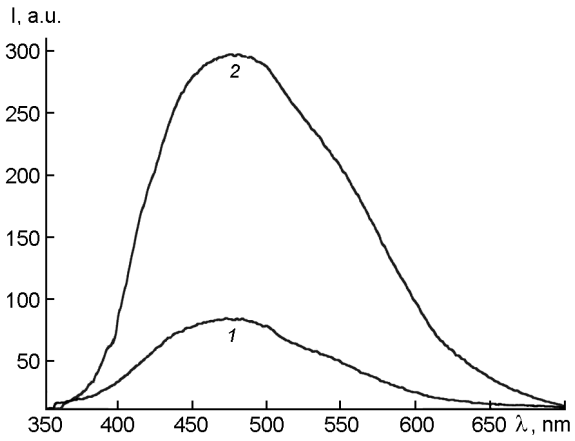

Fig. 4. X-ray luminescence spectra: (*1*) — $ZnWO_4$ film; (*2*) — bulk $ZnWO_4$.

broad emission band near 490 nm, which is typical for $ZnWO_4$ [1, 19–21].

The photoluminescence spectral characteristics of $ZnWO_4$ film produced by hydrothermal method in comparison with bulk $ZnWO_4$ are shown in Fig. 3. In Fig. 4 the X-ray luminescence spectra of $ZnWO_4$ bulk and film are presented. As follows from the data presented in Fig. 3 and Fig. 4 luminescent properties of $ZnWO_4$ film and bulk are similar. Both the bulk and film exhibit broad blue-green emission band peaked at 490 nm, as well as yellow band at about 550–580 nm. According to the data published in [21] emission band at ~490 nm is determined by charge-transfer transitions between the oxygen 2*p* orbitals and the empty *d* orbitals of the central W ion in a octahedral WO_6 complex. In the works [18, 20, 21] emission peak position at 550–580 nm is ascribed to defect tungstate group with oxygen vacancies.

4. Conclusions

Hydrothermal synthesis is widely used to produce nanorods and nanoparticles of zinc tungstate. In this work the hydrothermal method was developed to produce thick (10–20 μm) luminescent $ZnWO_4$ films.

The films obtained by this method possess wolframite structure. The luminescent properties of $ZnWO_4$ are a result of this wolframite structure, so the produced films demonstrate luminescent characteristics similar to the bulk material.

The technique applied in this work for the films production is quite simple and doesn't require any additional treatments of samples. We suppose that next efforts should be directed to improvements of this method for achievement of morphology homogeneity and proper phase composition of the samples.

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Люмінесцентні плівки $ZnWO_4$, отримані гідротермальним методом

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Плівки $ZnWO_4$ товщиною 10–20 мкм можуть бути отримані методом гідротермального синтезу без додаткової подальшої обробки. Отримані дані показують, що плівки мають структуру вольфраміту та демонструють люмінесцентні властивості, аналогічні об'ємному $ZnWO_4$.