

Nanocrystalline zinc and cadmium tungstates: morphology, luminescent and scintillation properties

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Nanosized crystals of zinc tungstate ($ZnWO_4$) were obtained in the form of elongated grains of width 30–40 nm and lengths up to 80 nm and nanorods of cadmium ($CdWO_4$) of width 25–30 nm and lengths up to 120 nm. The molten salt method in $LiNO_3$ at a low temperature was used. It was shown that the scintillation materials based on nano-sized crystalline powders of zinc tungstate have light output comparable with single crystals (~80 %) and have improved kinetic characteristics of luminescence (afterglow 0.07 % after 3 ms and 0.05 % after 20 ms). The possibility of obtaining composite films based on nanocrystalline $ZnWO_4$ and polymer matrix is discussed. Their main application area is the detectors for computed tomography.

Низкотемпературным методом в расплаве $LiNO_3$ получены наноразмерные кристаллы вольфрамата цинка ($ZnWO_4$) в виде продолговатых зерен шириной 30–40 нм и длиной до 80 нм и наностержни кадмия ($CdWO_4$) шириной 25–30 нм и длиной до 120 нм. Установлено, что сцинтилляционные материалы на основе наноразмерных кристаллических порошков вольфрамов цинка имеют световой выход, соизмеримый с монокристаллами (~ 80 %), и обладают улучшенными кинетическими характеристиками высвечивания (послесвечение 0,07 % через 3 мс и 0,05 % через 20 мс). Показана принципиальная возможность получения композитной пленки "нанокристаллический сцинтилятор $ZnWO_4$ — полимерная матрица", которая может быть использована в детекторах для компьютерной томографии.

1. Introduction

Single crystals of zinc tungstate $ZnWO_4$ (ZWO) and cadmium tungstate $CdWO_4$ (CWO) prepared by the Czochralski method from a melt are widely used as scintillation materials in detection and spectroscopic systems for nuclear physics and nuclear energetic. They are also widely utilized in tomography and X-ray scanning systems [1 – 3]. Furthermore, crystals of zinc tungstate are attractive as material for cryogenic phonon scintillation detectors. Due to low intrinsic

radioactivity they can be also used for registration of rare events such as 2β -decay of nuclei, radioactive decay of isotopes with very long lifetime, and interaction with non-baryonic dark matter [4].

The production of nanosized scintillators is a topical problem today. Their scintillation parameters may differ significantly from the bulk scintillators due to behavior of electronic and atomic excitations created by ionizing radiation in nanoscale solids [5]. In addition, production of nanocrystalline materials is technologically much simpler

than growth of bulk crystals by melts methods [6–10].

The most straightforward synthesis of nanocrystalline materials is the low-temperature method in molten inorganic salts as a reaction medium, which can provide a controlled size distribution of particles with unique morphology [6]. The molten salt synthesis method does not require any special expensive equipment and can be characterized by a short period of heat treatment. Correlation of the fusion time and weight ratio between the salt and basic substance allows to control morphology and size of the product [6–9].

The reactions are usually controlled by chemical equilibria in the melt. They are much faster than the diffusion-controlled solid-state reactions. The use of molten alkali metal nitrates is justified by the low cost of the reagents. Molten salts accelerate the diffusion of ions in the mixture and decrease the free energy of phase formation of crystallites, and hence reduce the overall temperature of the heat treatment. This allows to avoid the sublimation of volatile components of the initial mixture during the synthesis process [9, 10]. It should be noticed that single-phase of nanocrystalline zinc tungstate is formed at temperatures above 500°C at a normal pressure [11]. Products of the molten salt synthesis are not worse to materials obtained by more complex hydrothermal or microwave synthesis (in self-generated high pressure) by photoluminescent characteristics [11–13]. Furthermore the scintillation characteristics of these nanoparticles are absent.

The aim of this work is to synthesize the nanocrystalline compounds of zinc and cadmium tungstate with a homogeneous chemical composition and to study of their optical and scintillation properties.

2. Experimental

We used the following initial materials: $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ of analytical grade purity (98 %); LiNO_3 was prepared by dissolving the powder of Li_2CO_3 of analytical grade purity in an aqueous solution of HNO_3 ($\rho = 1.40$) (Merk, GR for analysis).

The synthesis process was carried out in two stages. Initially, the amorphous ZnWO_4 was prepared by co-precipitation of 1 M aqueous solutions of $\text{Zn}(\text{NO}_3)_2$ and Na_2WO_4 at room temperature with constant stirring (Fig. 1a). Then the white precipitate was dried at 70°C in air and mixed with lithium

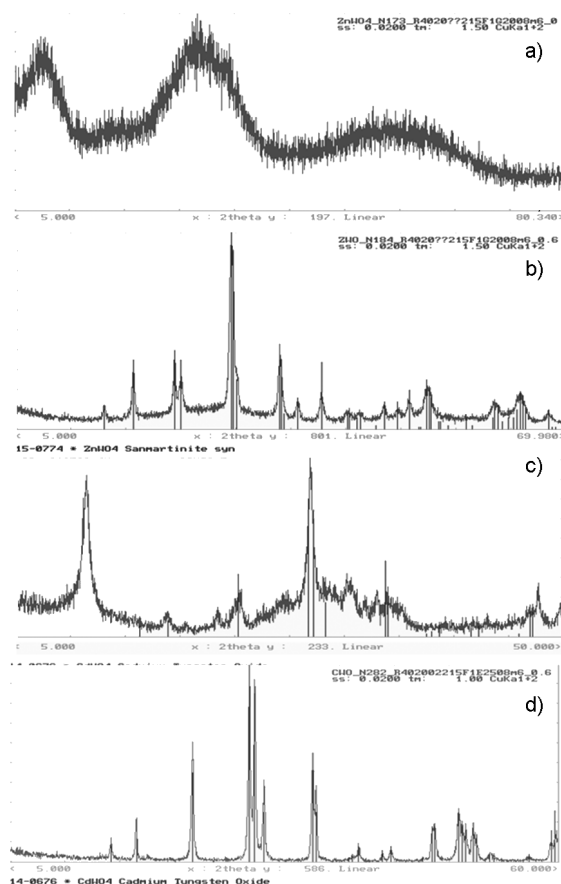


Fig. 1. X-ray diffraction of powders obtained under different conditions: a) ZnWO_4 — co-precipitation from the aqueous phase; b) ZnWO_4 — from amorphous powder (a) in the melt of LiNO_3 ; c) CdWO_4 — co-precipitation from the aqueous phase; d) CdWO_4 — from powder (c) in the melt of LiNO_3 .

nitrate in a weight ratio of 1:10. The mixture was calcined at 270°C for 6 h in ceramic crucible. The product was washed by distilled water and ethanol several times, filtered and dried at 70°C in air for 3 h. X-ray diffraction of nanocrystalline ZnWO_4 showed in Fig. 1b.

Nanocrystalline cadmium tungstate was prepared by a similar way. Co-precipitation of 0.1 M aqueous solutions of cadmium nitrate and sodium tungstate were carried out at room temperature and constant stirring. The product was heterogeneous in composition, but nanocrystalline monoclinic CdWO_4 was a dominated phase (Fig. 1c). Product was mixed with the lithium nitrate in a weight ratio of 1:10 after drying at 70°C in air. The mixture was calcined at 270°C for 8 h in ceramic crucible. The product of the synthesis (nanocrystalline CdWO_4 with

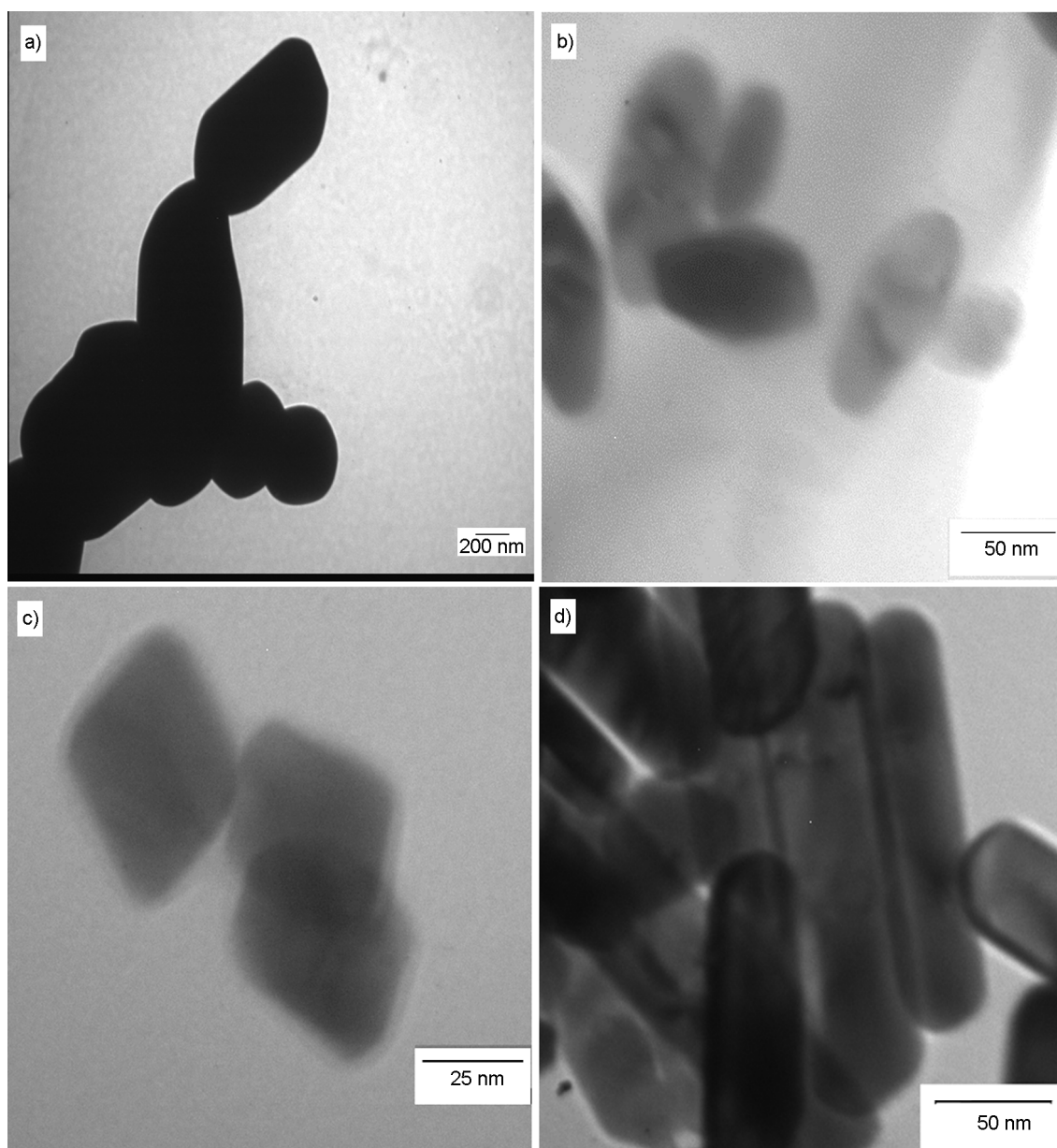


Fig. 2. Electron microscopy image: a) ZnWO_4 particles, obtained by solid-phase synthesis at $T = 900^\circ\text{C}$; b) ZnWO_4 nanoparticles, obtained in LiNO_3 melt at $T = 270^\circ\text{C}$; c) ZnWO_4 nanoparticles, obtained in LiNO_3 melt at $T = 400^\circ\text{C}$; d) CdWO_4 nanorods, obtained in LiNO_3 melt at $T = 270^\circ\text{C}$.

structure of wolframite (Fig. 1d)) was washed by distilled water and ethanol several times, filtered and dried at 70°C in air for 3 h.

XRD analysis of the samples showed the absence of significant changes in the intensities of the XRD bands when we vary the amount of lithium nitrate and base substance or ZnWO_4 or CdWO_4 .

Lithium nitrate was chosen as the molten salt due to a sufficiently low melting point (253°C) [3, 7, 9, 14]. It was taken into account that the doping of CdWO_4 with Li^+ ions

up to 3 at.% causes increment in photoluminescence intensity, while the doping with Na^+ ions causes the opposite effect [3, 14].

Optical-luminescence properties were measured on samples of 2 mm films prepared by addition nanocrystalline ZnWO_4 or CdWO_4 to polymerized transparent organosilicic rubber in a weight ratio of 3:5. Similarly prepared films obtained by the introduction of solid-state synthesized powders (size ~ 400 nm (Fig. 2a)) and scattered crystals of ZnWO_4 (< 250 μm) were used for comparison of optical-luminescence proper-

ties. X-ray luminescence spectra were measured by spectrophotometric complex KSVU-23. X-ray source REIS ($U_\alpha \leq 40$ kV, $i_a \leq 50$ μ A) was used as an excitation. Afterglow level ($\eta(\%)$) was measured with a measuring-computing system for the study of kinetic characteristics (IVKK). The light output of the samples was determined by the current method with X-ray excitation source IRI ($U_\alpha = 100$ kV, $i_a = 1$ mA) [15]. The luminescence decay time was measured using the method of correlated in time counting individual photons. Excitation of luminescence of the samples was carried out the fourth harmonic of YAG:Nd laser (266 nm). FEU-136 used as photodetector.

Morphology of the nanocrystals was determined by transmission electron microscopy using microscope EM-125 (SELMA, Ukraine). Electron accelerating voltage was 125 kV, the survey was carried out in the bright field mode, the image recorded by CCD matrix. We used thin carbon films coated with water suspension of the investigated powders for electron microscopy.

Phase purities of the samples were characterized by X-ray diffraction (XRD) on Siemens D 500 powder diffractometer (radiation $\text{CuK}\alpha$, nickel filter, Bragg-Brentano geometry). Diffraction patterns were measured in the angular range $5 < 2\theta < 90^\circ$ with increments of 0.02° and accumulation time 2 s at each point. Search of the phases was executed on the catalog PDF-1 [16] using the software EVA and SEARCH, included in the diffractometer.

3. Results and discussion

Morphology and size of the crystal grains were measured by electron microscopy. Nanosized monoclinic ZnWO_4 in the form of elongated grains of width 30–40 nm and of length up to 80 nm (Fig. 2b) was obtained by chosen method of synthesis (see Experimental part). Faceted crystallites were obtained when temperature of the melt was raised up to 400°C during 8 h (Fig. 2c). The typical form of crystallites for CdWO_4 is an elongated nanorod of width 25–30 nm and of length up to 120 nm (Fig. 2d). XRD analysis confirmed the results concerning the size of the crystallites and identified the samples as a monoclinic lattice with the structure of wolframite (Fig. 1b, 1d).

X-ray luminescence spectrum of nanosized ZnWO_4 is similar to the spectrum of single-crystal and has a broad band with $\lambda_{max} = 480$ nm (Fig. 3a). X-ray spectrum of

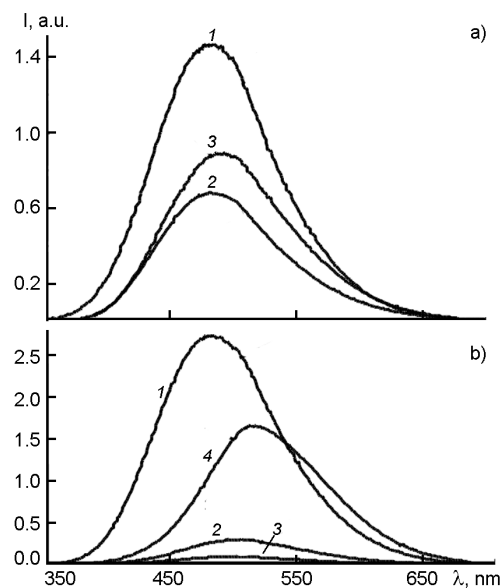


Fig. 3. The spectra of X-ray luminescence: a) ZnWO_4 samples: 1 — single crystal; 2 — product of solid-phase synthesis; 3 — nanosized crystalline sample (signal for powder obtained by co-precipitation from aqueous solutions are absent); b) CdWO_4 samples: 1 — single crystal; 2 — product of solid-phase synthesis; 3 — the original powder obtained by co-precipitation from aqueous solutions of corresponding salts, 4 — nanosized crystalline sample.

CdWO_4 is shifted toward the longer wavelengths by ~ 20 nm (Fig. 3b). This result is in good agreement with published data [17].

Luminescent properties of ZnWO_4 and CdWO_4 particles are similar and are caused by the transitions within oxyanion complex [12, 18, 19]. In the work [19] emission peak position at 500 nm was associated with transitions in tungstate group WO_6^{6-} and emission with $\lambda_{max} = 570\text{--}580$ nm was associated with defect tungstate group with oxygen vacancies [19]. The ratio of contributions from main and defect bands determines the maximum of integral luminescence band. So, the red shift of the emission peak position for CdWO_4 indicates the presence of significant number of defect luminescence centers. This phenomenon was observed for the nanorods obtained by hydrothermal synthesis [17]. We believe, however, that it may be a result of the CdWO_4 morphology.

Measurements of scintillation parameters showed the following results. Nanocrystalline samples ZnWO_4 have light output comparable to the single crystal (~ 0.8 from

Table 1. Optical and kinetic properties ZnWO₄ and CdWO₄

Sample	Dimensions of grains	Light output, a. u.	Decay time, μ s	Afterglow, %				
				3 ms	5 ms	10 ms	15 ms	20 ms
Crushed single crystal ZnWO ₄ (etalon)	<250 μ m	1	–	0.14	0.103	0.068	0.053	0.045
Nanosized crystal ZnWO ₄	~20–50 nm	0.81	27	0.072	0.064	0.055	0.05	0.047
Nanosized crystal CdWO ₄	~20–70 nm	–	–	0.027	0.021	0.015	0.012	0.01
Solid phase synthesis product ZnWO ₄	~0.4–1.0 μ m	0.61	21	0.858	0.747	0.618	0.553	0.512

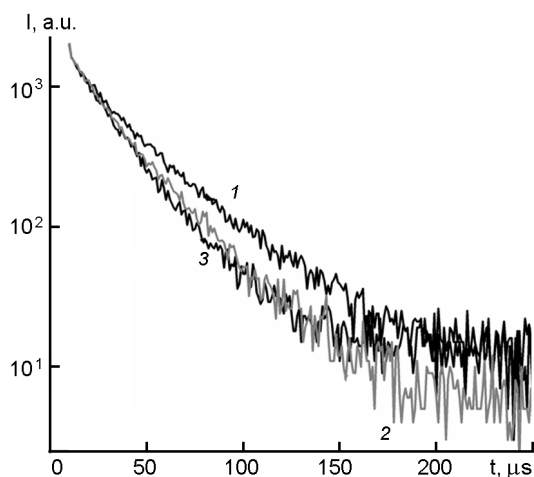


Fig. 4. Luminescence decay time for ZnWO₄: 1 — nano-sized crystalline sample; 2 — product of solid-phase synthesis; 3 — single crystal.

crushed crystal). At the same time, kinetic characteristics of luminescence decay are improved in comparison with single crystals. The afterglow level of nanocrystalline ZnWO₄ and CdWO₄ in the time range from 3 to 20 ms (the most important range for computer tomography) is lower than in crushed single crystals (see Table) and is close to ~ 0.05 %. Decay time for all the samples of ZnWO₄ was approximately identical and was about 20–30 μ s (Fig. 4).

The high conversion efficiency and low afterglow of nanocrystalline ZnWO₄ makes it promising material for digital X-ray tomography. In particular, it can be used in the form of a composite film "nanocrystalline scintillator ZnWO₄ — polymer matrix" which was used in the present study. Using such film, the detection surface can be made much larger than for single crystal detector. In addition, the scintillator made of dispersed substance provides better uniformity of the light output which is very important for computer tomography applications. We confirmed this statement by

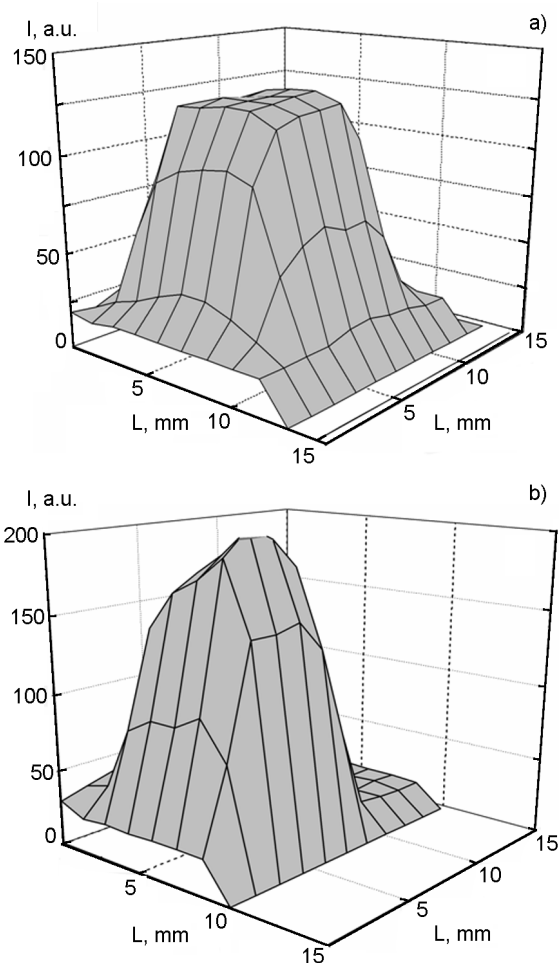


Fig. 5. Distribution of the light output for area: a) composite scintillation films based on ZnWO₄ nanocrystalline; b) polished ZnWO₄ single crystal.

measuring the distribution of the light output over the surface for the composite scintillator film (Fig. 5a) and for the polished single crystal (Fig. 5b). Output parameters of such detector can be further improved by selecting the optimum composition of polymer compositions, component concentrations and other process parameters.

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4. Conclusions

Nanosized crystals of zinc and cadmium tungstates are obtained using the method of co-deposition from aqueous solutions of the salts. The melting inorganic salts were used for crystallization.

We showed a possibility of obtaining the scintillation materials based on nano-sized crystalline powders of zinc tungstate with light output comparable to single crystals (~80 %) and with improved kinetic characteristics of luminescence (afterglow 0.07 % after 3 ms and 0.05 % after 20 ms). For afterglow is 0.01 % after 20 ms.

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Нанокристалічні вольфрамати цинку та кадмію: морфологія, люмінесцентні та сцинтиляційні властивості

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Низькотемпературним методом у розплаві LiNO_3 одержано нанорозмірні кристали вольфраму цинку (ZnWO_4) у вигляді довгастих зерен шириною 30–40 нм і довжиною до 80 нм і наностержні кадмію (CdWO_4) шириною 25–30 нм і довжиною до 120 нм. Встановлено, що сцинтиляційні матеріали на основі нанорозмірних кристалічних порошків вольфраматів цинку мають світловий вихід, сумірний з монокристалічними (~80 %), і характеризуються поліпшеними кінетичними характеристиками висвічування (післясвітіння 0,07 % через 3 мс і 0,05 % через 20 мс). Показано принципову можливість одержання композитної плівки "нанокристалічних сцинтиляторів ZnWO_4 — полімерна матриця", яка може бути використана у детекторах для комп'ютерної томографії.