



Influence of grain size on luminescence properties of micro- and nanopowder $Zn_2V_2O_7$ vanadate



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HIGHLIGHTS

- Spongiform nanocrystalline α - $Zn_2V_2O_7$ was synthesized.
- Grain size of α - $Zn_2V_2O_7$ influence its luminescence properties.
- The lattice parameters of α - $Zn_2V_2O_7$ depend on the grain size in submicron range.

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ABSTRACT

Micro- and spongiform nanocrystalline $Zn_2V_2O_7$ compounds were synthesized by hydrothermal and solid-state reaction techniques, and their morphological features were investigated by scanning electron microscopy (SEM). The grain size ranges of the produced powders were 3–15, 0.5–2 μ m, and 50–500 nm. The luminescence spectra of these compounds were measured under pulse cathode beam and photoexcitation (200–400 nm). The luminescence decay properties of $Zn_2V_2O_7$ were studied.

It is found that the intensity, maximum position of luminescence spectra and luminescence decay time of $Zn_2V_2O_7$ samples depend considerably on the grain size of the synthesized powders. The processes of energy relaxation in $Zn_2V_2O_7$ and the observed size effect on the luminescence properties are also discussed.

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1. Introduction

Zinc pyrovanadate ($Zn_2V_2O_7$) is a promising multifunctional compound. A number of studies confirm the possibility of practical application of $Zn_2V_2O_7$ to create functional materials for lithium batteries (Chen et al., 2013) and photocatalysis (Abraham et al., 2014; Pei et al., 2015). Investigations of luminescent properties of zinc pyrovanadate have attracted considerable attention of researchers due to its strong self-activated broad-band luminescence, conversion properties of ultraviolet (UV) radiation in the yellow-green region of the visible spectrum, and various synthesis techniques. These types of compounds are promising for use as phosphors for white light-emitting diodes (WLEDs) with the blue or near-UV excitation (Kuang et al., 2013; Guan et al., 2014; Butt

et al., 2015).

A topical direction for the investigation of modern phosphor compounds and scintillation materials is the observation and finding of applications of the well-known with nanometer and submicron grain size (Lisitsyn et al., 2014; Sadhu et al., 2007; Roco et al., 2011; Feng and Xu, 2001; Yakubovskaya et al., 2011). In this study, we present the results of investigations of radio- and photoluminescence (PL) properties of $Zn_2V_2O_7$ samples synthesized by three different techniques. The synthesized vanadate samples have different grain sizes. The goal of this study is to determine the size effect of zinc pyrovanadate.

2. Materials and methods

2.1. Experimental set-up

$Zn_2V_2O_7$ samples were synthesized using an Ural-Gefest microwave heater (2.5 GHz, 750 W) and muffle furnace (SNOL,

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2.2 kW).

Phase composition of the synthesized samples was analyzed by X-ray diffraction (XRD) technique using DRON-UM-1 (CuK_α). Grain size and morphology of the samples were determined by a SEM (Zeiss Sigma VP).

PL and photoluminescence excitation (PLE) spectra of the samples were measured using a PerkinElmer LS-55 fluorescence spectrometer. The excitation of luminescence was performed using a pulse xenon lamp (220–450 nm) and the corresponding spectra were recorded on a Hamamatsu photomultiplier R8630 (standard PMT for LS-55 with sensitivity region 200–650 nm).

Pulse cathode luminescence (PCL) spectra were measured using KLAVI-R setup (energy, 150 keV; beam current density, 150 A/cm²; pulse duration, 2 ns) equipped with a charge-coupled device (CCD) linear sensor and image intensifier (400–850 nm) at room temperature.

The decay curves were measured using a pulse cathode source MIRA-2D (energy, 200 keV; pulse duration, 20 ns) with photomultiplier FEU-97, and the curves were recorded on a Tektronix TDS5034B oscilloscope with 300-k Ω load resistor.

2.2. Sample preparation

Single-phase $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ samples were obtained by three ways: from the oxides by solid-state technique (Sample #1); from the precursor in a microwave oven (Sample #2); and by heat-treating the same precursor in a muffle furnace (Sample #3).

The solid-state synthesis of Sample #1 was performed in the temperature range of 550–590 °C. ZnO (99%) and V₂O₅ (99%) were used as raw materials. The stoichiometric mixture of these materials was calcined several times with intermediate regrinding. Finally, the sample was annealed for 50 h at 590 °C.

For the synthesis of Samples #2 and #3, we used the method of precursor preparation by evaporating the stoichiometric mixture of the starting colorless solutions Zn(NO₃)₂ and NH₄VO₃. An advantage of this technique when compared with the method proposed by Abraham et al. (2014) is the absence of chlorine and carbon ions in the precursor, which can produce uncontrolled changes in the oxidation state of vanadium ions in the reaction product. The precursor appeared as a fine pink powder when dried at 110 °C. For the synthesis of Sample #2, the dried precursor was irradiated with electromagnetic waves in a microwave oven at 590 °C with a heating rate of 10 °C/min, synthesis time of 45 min, and cooling time of 2 h. Sample #3 was obtained by precursor annealing at 300 °C for 20 h. Additional annealing at 500 °C for 90 h resulted in the generation of the single-phase sample.

Phase composition and purity of all synthesized samples were verified by XRD and energy-dispersive spectroscopy (EDS) techniques. The synthesized $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ samples were monoclinic with space group C2/c. The lattice parameters of the samples calculated using XRD data are presented in Table 1. It is shown in the table that the unit cell parameters of the samples slightly differed from each other.

Table 1
Lattice parameters of $\text{Zn}_2\text{V}_2\text{O}_7$ samples.

Lattice parameters	Sample #1	Sample #2	Sample #3
<i>a</i> (Å)	7.433	7.434	7.425
<i>b</i> (Å)	8.326	8.321	8.324
<i>c</i> (Å)	10.130	10.120	10.122
β (°)	111.76	111.82	111.78
<i>V</i> (Å ³)	582.18	581.17	580.93

2.3. SEM analysis

SEM analysis was performed by dispersing the powder samples on a carbon-conductive duct tape (Figs. 1 and 2). The average grain size of Samples #1 and #2 were found to be in the range of 3–15 and 0.5–2 μm , respectively. The grains of Samples #1 and #2 have a round form, whereas Sample #3 has agglomerated spongiform grains with size of 1–3 μm , which are formed by nanoparticles with size ranging from 50 to 500 nm.

3. Results and discussion

3.1. PL properties

The PL and PLE spectra of the synthesized $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ samples are presented in Fig. 3. The PL spectra (Fig. 3b) show that the $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ samples have a wide range of luminescence with a maximum peak at 535 nm (full-width at half-maximum (FWHM) 100 nm) under UV excitation. The spectra are very similar to each other, but Sample #1 has an additional band of luminescence near 450 nm. The intensity of luminescence spectra of Sample #1 is rather lower than that of the other samples.

The PLE spectra (Fig. 3a) of $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ recorded at 535 nm are the multiband spectra with relatively narrow band having the maximum at 330 nm. It is observed from the figure that the intensity of the band at 330 nm significantly changes relatively the intensity of the other bands in the range below 315 nm. The ratio of intensities of the aforementioned bands in PLE spectra is found to decrease with decreasing grain size of the samples. Such behavior of PLE spectra for $\text{Zn}_2\text{V}_2\text{O}_7$ and other vanadate systems is unusual. The origin of PLE and PL spectra is discussed in Section 3.4.

3.2. PCL properties

The equipment for PL measurements has a limited range in the red region of luminescence spectra (200–650 nm); therefore, we carried out additional measurements using the PCL equipment (400–850 nm), whose spectra are presented in Fig. 4. It is evident from the figure that the intensity and maximum position of the PCL spectra depend on the type of $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ sample. Therefore, the PCL spectra of Sample #1, which synthesized by solid-state reaction, have the lowest intensity of PCL (~4–4.5 times the PCL intensity of the precursor-synthesized samples) and the maximum position at 545 nm. Samples #2 and #3 have a highest PCL intensity and the maximum positions of their PCL spectra are located at 560 and 570 nm, respectively. These results show that the luminescence properties of $\alpha\text{-Zn}_2\text{V}_2\text{O}_7$ highly depend on grain size, and that the luminescence intensity increases with decreasing grain size.

It should be noted that the mismatch of between the positions of the maxima and the absence of shift of maxima with grain size in contrast to PCL spectra could be explained by the different spectral sensitivity of the setup used. The PCL spectra are the closest to the true spectra because of their better sensitivity in the red region.

3.3. Decay luminescence properties

Decay curves of the synthesized samples were measured in the band at 550 nm (Fig. 5). It is observed from the figure that the decay curves are nonelementary and consist at least of two components. The best approximation of these curves has been achieved using the superposition of two exponential functions:

$$I(t) = A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}},$$

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