# Properties of the nanosized zinc pyrovanadate synthesized by mechanochemical, barothermal and ultrasonic methods

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In recent years $Zn_3V_2O_8$ has attracted a lot of attention as an effective catalyst for selective oxidation of glucose to galacturonic acid and as highly sensitive material for detecting acetone in air. $Zn_3V_2O_8$ is a promising phosphor with broadband emission from 400 nm to more than 800 nm. The color of the luminescent materials ranged from green to yellow-orange via white. In addition, $Zn_3V_2O_8$ does not contain rare earth elements and cheaper than the traditional phosphor materials. But traditional methods for synthesizing of zinc pyrovanadate have some efficiency problems and are not eco-friendly. Currently, zinc pyrovanadate is synthesized by two conventional methods: i) – co-precipitation method synthesis from soluble salts leads to formation nano-plate structure but accompanied by pollution a large amount of water, ii) – solid state synthesis from salts or oxides, requires high temperatures and a long time synthesis. Moreover, solid state synthesis doesn't lead to formation nanostructures.

**Synthesis:**

For all syntheses powders of initial ZnO and $V_2O_5$ oxides with molar ratio 3:1 were used. XRD of the initial oxides is shown in Fig.1. SEM image demonstrates the presence of large particle of $V_2O_5$ surrounded of small particles of ZnO (Fig.2).

1) Mechanochemical (MCh) synthesis was realized in a planetary ball mill in aqueous medium during 20 min with rotation frequency – 500 rpm.

2) Barothermal (BT) synthesis was carried out into a steel autoclave with Teflon lining in aqueous medium at 150°C for 1 h.

3) Ultrasonic (US) treatment was carried out by UZDN-A at a frequency of 22 kHz in aqueous medium for 20 min at room temperature.

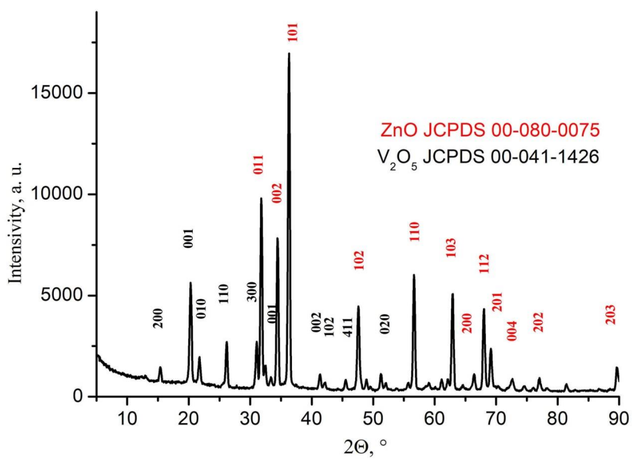


Fig.1. XRD data of initial mixture ZnO and $V_2O_5$

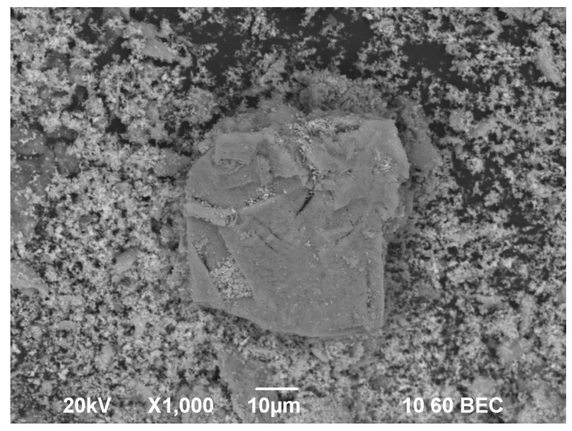


Fig.2. SEM image of initial mixture ZnO and $V_2O_5$

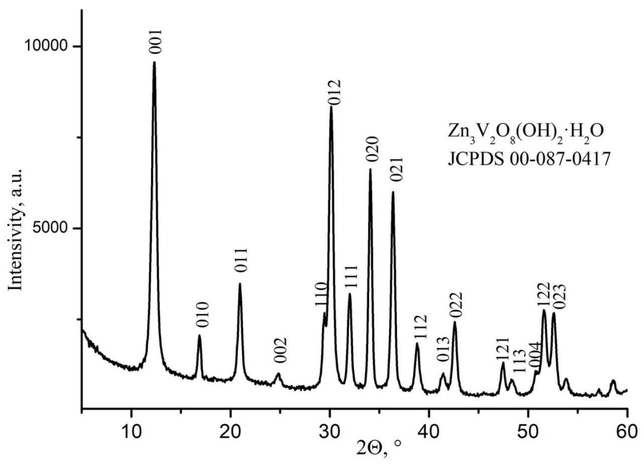


Fig.3. XRD data of ZnO and $V_2O_5$ after US treatment

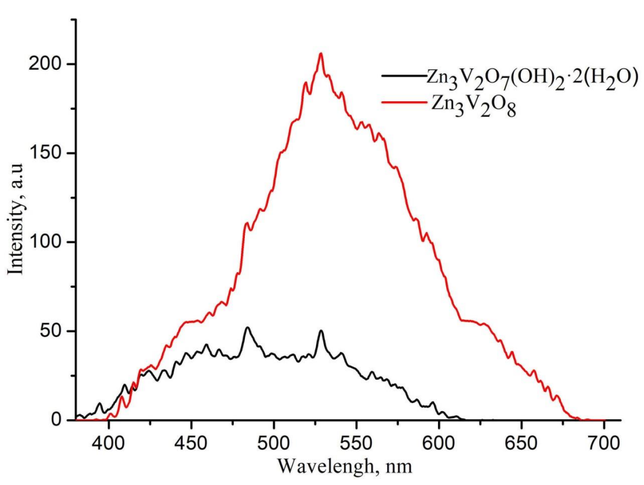


Fig.5 PL spectra of $Zn_3V_2O_7(OH)_2$ $2(H_2O)$ and $Zn_3V_2O_8$ ($\lambda_{ex}$ = 360 nm).

## Results and discussion

Mechanochemical, Barothermal and Ultrasonic treatments of oxides in aqueous medium lead to formation of $Zn_3V_2O_7(OH)_2·2(H_2O)$ phase. XRD data of ZnO and $V_2O_5$ after US treatment during 20 min is presented in Fig.3. No reflections of the initial oxides (Fig.1) were found in the final product. DTA shows a loss of crystalline water up to 300°C with the formation of $Zn_3V_2O_8$, which is confirmed by XRD analysis. The SEM and TEM images show that $Zn_3V_2O_7(OH)_2$ $2(H_2O)$, obtained by MCh, US and BT syntheses has the morphology of thin nanoplatelets forming agglomerates, and particles with the morphology of the initial oxides are completely absent (Fig.4). The morphology of zinc pyrovanadate similar to morphology of samples synthesized by conventional co-precipitation method. Samples synthesized by US and BT methods have plate morphology with average diameter about 1 μm and thickness about 50 nm (Fig.4 (a,b,d)). The sample synthesized by MCh method also has plate morphology but with a smaller size 0,3-0.5μm and a thickness of about 50 nm (Fig.4 (c)).

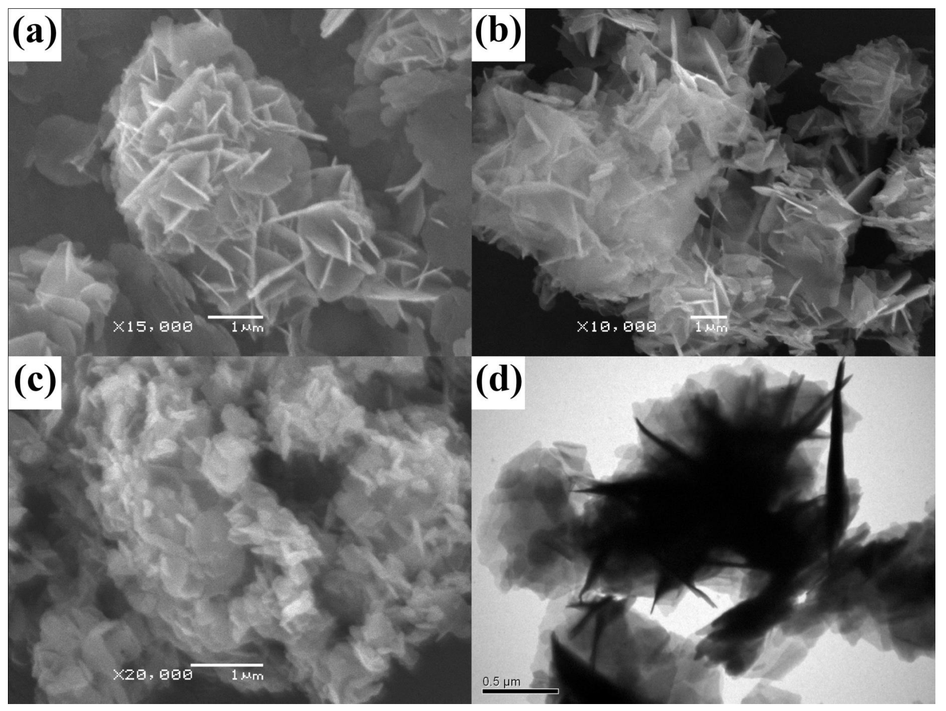


Fig.4., SEM images of ZnO and $V_2O_5$ after (a) US, (b) BT and (c) MCh treatment, (d) TEM image of $Zn_3V_2O_7(OH)_2·2(H_2O)$

PL spectra were measured at excitation wavelength 360 nm. Fig.5 shows the PL spectra of $Zn_3V_2O_7(OH)_2·2(H_2O)$ and $Zn_3V_2O_8$ obtained by US syntheses. PL spectra $Zn_3V_2O_8$ have intense broadband emission from 400 nm to 700 nm with a maximum at 540 nm, which corresponds to the sensitivity spectrum of the human eye. The phosphor properties of zinc pyrovanadate strongly depend on the presence of crystalline water in its structure.

## Conclusions

Mechanochemical, Barothermal and Ultrasonic treatments make it possible to carry out the low-temperature synthesis of zinc pyrovanadate from oxides. These methods of synthesis are energy efficient, fast, eco-friendly and make it possible to obtain nanoplate structure. Zinc pyrovanadate showed photoluminescent emission in range from 400 to 700 nm, which corresponds to the sensitivity spectrum of the human eye.