Properties of nanosized $ZnMoO_4$ synthesized by conventional, hydrothermal and ultrasonic methods

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Background The $ZnMoO_4$ is perspective material for bolometers, scintillation detectors, humidity sensors, microwave dielectric devices, battery electrodes and high effective catalyst oxidation ethanol to acetaldehyde. The traditional method of synthesis of the $ZnMoO_4$ is based on the interaction of soluble salts which demand a lot of water. The aim of our work was to compare different methods of synthesis of the $ZnMoO_4$ and establish their advantages and disadvantages.

Conventional co-precipitation synthesis

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $Zn(NO_3)_2\cdot 6H_2O$, in an equimolar ratio of Mo-Zn, were solved in water, with added NH_4OH for precipitation, then added nitric acid for neutral medium. The precipitation was washed several times (during a week) for removing accompanying ions and dried at 100°C. XRD showed $Zn_5Mo_2O_{11}\cdot 5H_2O$ as single product (Fig.1) After hearted the samples at 300°C was detected a-$ZnMoO_4$ (Fig.2) although ZnO must be presented according to the equation: $Zn_5Mo_2O_{11}\cdot 5H_2O \rightarrow 2ZnMoO_4 + 3ZnO + 5H_2O$

CEM confirmed the formation of two phases: $ZnMoO_4$ with needle-like structure and ZnO with ball structure (Fig.3). So, this method of synthesis is not ecological friendly and and doesn`t lead to the formation of a pure a-$ZnMoO_4$ phase.

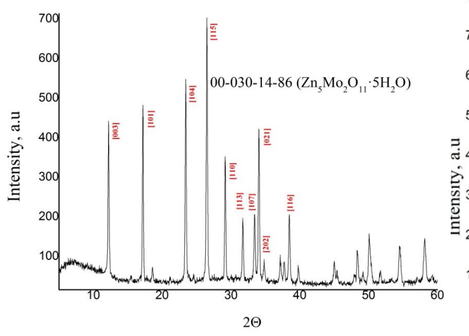


Fig.1. XRD data of $Zn_5Mo_2O_{11}\cdot 5H_2O$

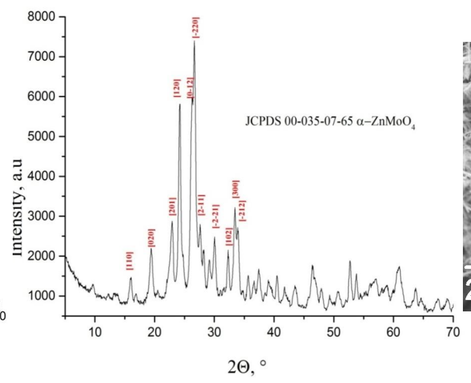


Fig.2. XRD data of $ZnMoO_4$

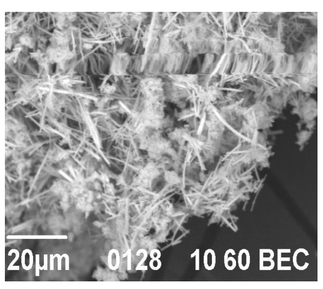


Fig.3. CEM data of $ZnMoO_4$ and ZnO

Conventional solid-state synthesis

ZnO and MoO_3 powders (1:1 molar ratio) were loaded into an agate mortar and grinded. The obtained mixture was transferred into alumina crucible and was calcinated at 900°C for 4 h.

a-$ZnMoO_4$ (Fig.4) obtained by solid-state reaction demonstrates non-uniform distribution of the elements (Fig. 5).

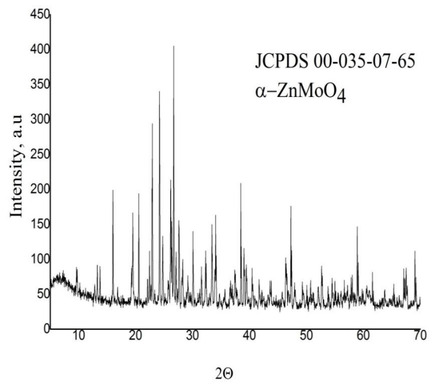
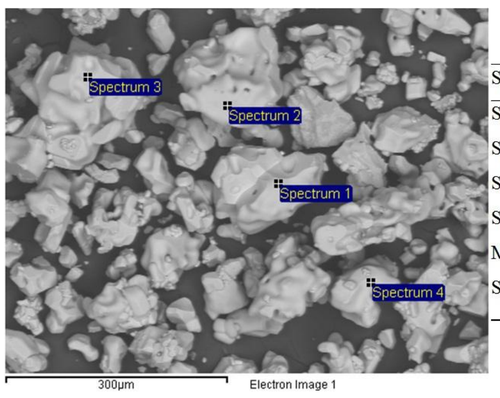


Fig.4. XRD data of $ZnMoO_4$



Spectrum	Zn	Mo	O
Spectrum 1	11.27	19.37	69.37
Spectrum 2	24.99	12.50	62.50
Spectrum 3	12.33	18.83	68.83
Spectrum 4	42.02	3.99	53.99
Mean	22.65	13.67	63.67
Std. deviation	14.34	7.17	7.17

Fig.5. CEM data of a-$ZnMoO_4$ synthesized by solid-state

Ultrasonic synthesis

Initial mixture of MoO_3 and ZnO in water medium was treated by ultrasound during 20 minutes at room temperature. X-ray diffraction analysis showed the phase $ZnMoO_4\cdot 0.8H_2O$ was formed (Fig.6) with interwoven nano-filamentary structures and uniform distribution of elements (Fig.7,8). After calcination at 300°C $ZnMoO_4\cdot 0.8H_2O$ returned into pure phase α-$ZnMoO_4$ with nanorod structure.

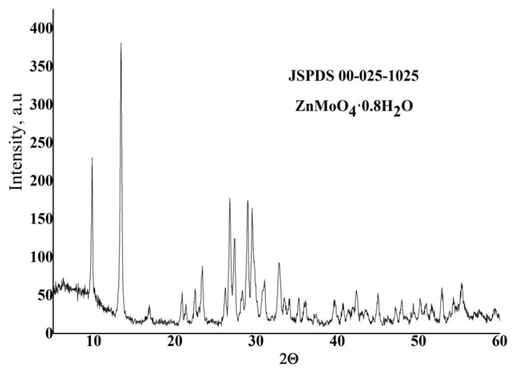


Fig.6. XRD data of $ZnMoO_4\cdot 0.8H_2O$

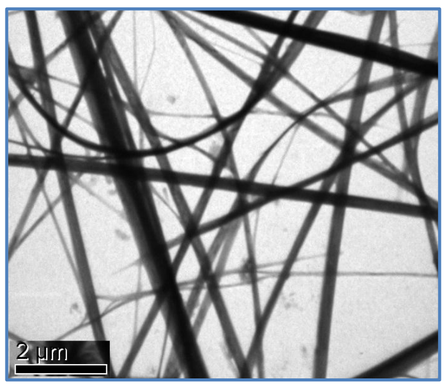
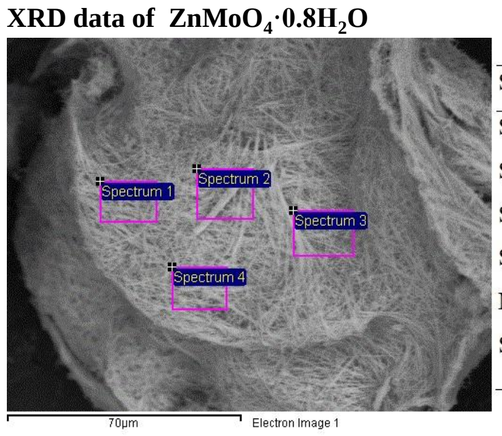


Fig.7. TEM data of $ZnMoO_4\cdot 0.8H_2O$



Spectrum	Zn	Mo	O
Spectrum 1	11.37	19.32	69.32
Spectrum 2	11.41	19.30	69.30
Spectrum 3	10.67	19.67	69.67
Spectrum 4	12.70	18.65	68.65
Mean	11.54	19.23	69.23
Std. deviation	0.85	0.42	0.42

Fig.8. CEM data of $ZnMoO_4\cdot 0.8H_2O$

Barothermal synthesis

Initial mixture of MoO_3 and ZnO in water medium were loaded in teflon-lined stainless steel autoclave and heated at 170°C for 1hour - XRD showed the formation $ZnMoO_4\cdot 0.8H_2O$ but reflections of initial MoO_3 were presented too (Fig.9). However, at three-hours synthesis at 170°C leads to formation single phase. $ZnMoO_4\cdot 0.8H_2O$ (Fig.10). In both case were formed particles with needle-like structure (TEM) Fig.11.

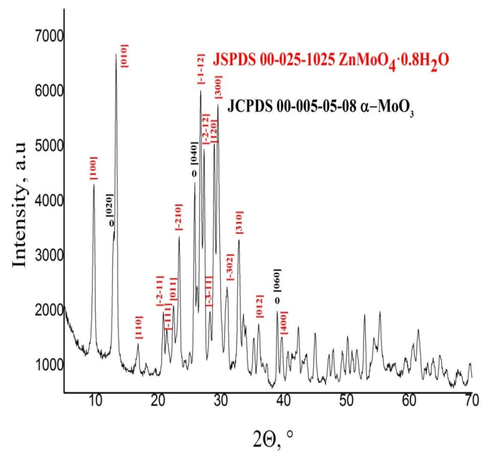


Fig.9. XRD data of $ZnMoO_4\cdot 0.8H_2O$ & MoO_3

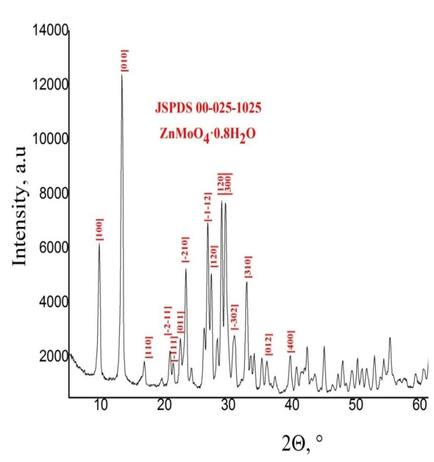


Fig.10. XRD data of $ZnMoO_4\cdot 0.8H_2O$

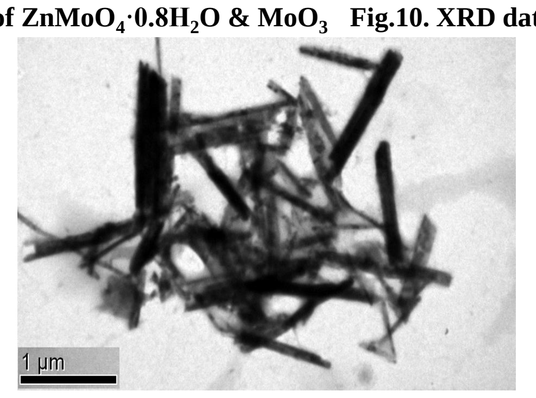


Fig.11. TEM data of $ZnMoO_4\cdot 0.8H_2O$

Conclusions The using of alternative methods of synthesis are perspective, eco-friendly direction. Thus, in contradistinction to conventional co-precipitation or solid-state syntheses the application of ultrasonic treatment or barothermal treatment of oxides in water medium lets to fast formed pure nanostructured $ZnMoO_4\cdot 0.8H_2O$ with high S_{BET}. The use of cheap oxides ZnO and MoO_3 as raw materials for synthesis $ZnMoO_4$ makes it possible to organize a closed cycle where water can be used in the next synthesis without purification. The most promising method of synthesis is ultrasonic treatment, which is needed just 20 minutes to formation the zinc molibdate phase.