Mechanochemical synthesis and characterization of $ZnMoO_4 \cdot 0{,}8H_2O$, and $ZnMoO_4$ nanostructures.

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The pollution of water is one of the ten major environmental issues, so development of eco-friendly synthesis methods is very important direction of modern chemistry. $ZnMoO_4$ is known as an industrial white pigment with anti-corrosion properties, and it is also a perspective material for bolometers, scintillation detectors, humidity sensors, microwave dielectric devices and as phosphor. Our previous studies have shown the possibility of formation of salts from poorly soluble oxides by ultrasound treatment [1]. This study showed possibility of formation of zinc molybdate from oxides by mechanochemical treatment.

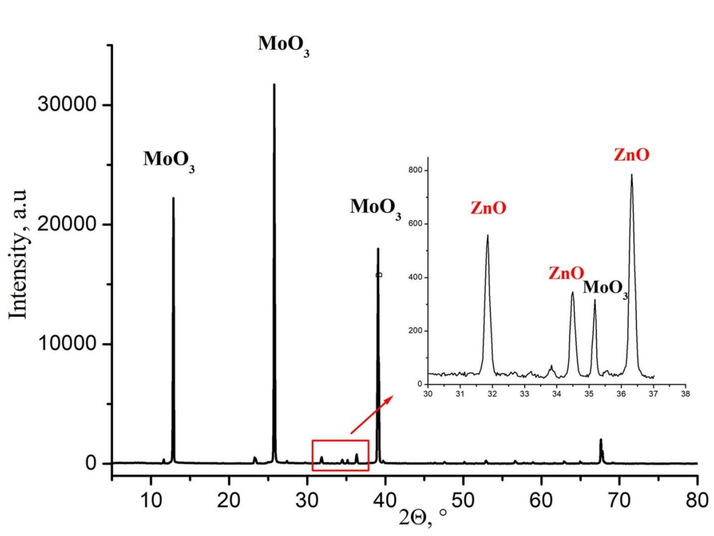

Fig.1. XRD data of initial mixture ZnO and MoO_3

Initial mixture of oxides ZnO and MoO_3

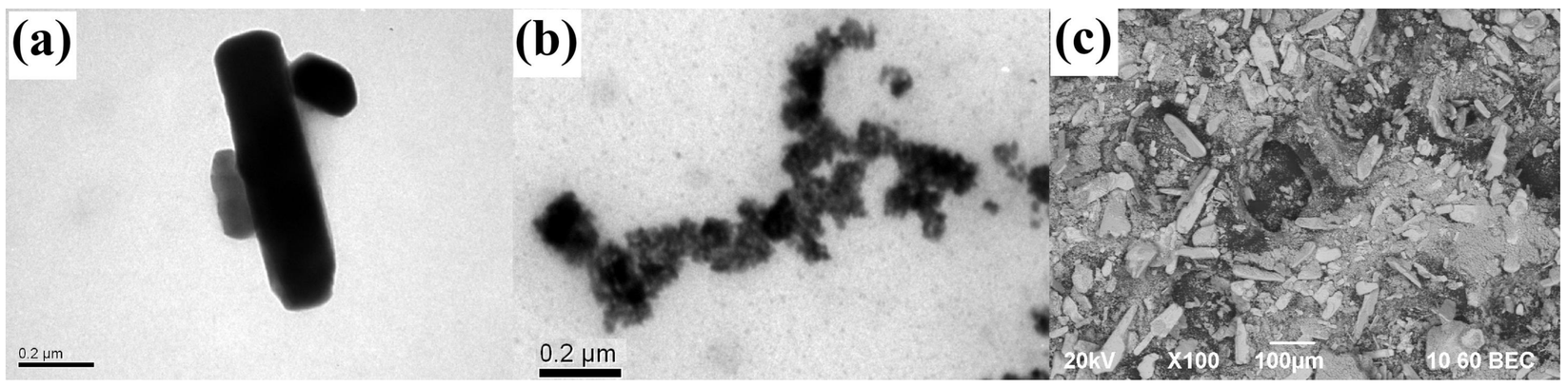

Fig.2. (a) TEM image MoO_3, (b) TEM image ZnO and (c) SEM images of initial oxides: MoO_3 and ZnO

Fig 1. shows XRD data of initial mixture of ZnO and MoO_3. The ratio of the most intense reflex of MoO_3 to most intense reflex of ZnO is 40. Crystallite sizes D_{MoO3} = 75 nm while D_{ZnO} = 23 nm. SEM and TEM images of initial mixture of oxides are presented in Fig. 2. Mixture of oxides consist of large particles of MoO_3 100 μm long and 20 μm wide. The size of ZnO particles becomes 50-20 nm.

Properties of $ZnMoO_4 \cdot 0{,}8H_2O$, and $ZnMoO_4$ nanostructures obtained by mechanochemical synthesis

Obtaining of zinc molybdate : The mechanochemical (MCh) treatment of initial mixture of ZnO and MoO_3 with molar ratio 1:1 was carried out in the planetary ball mill Pulverisette-6 (Fritsch) during 10 and 60 minutes in aqueous medium. The rotation frequency was 500 rpm.

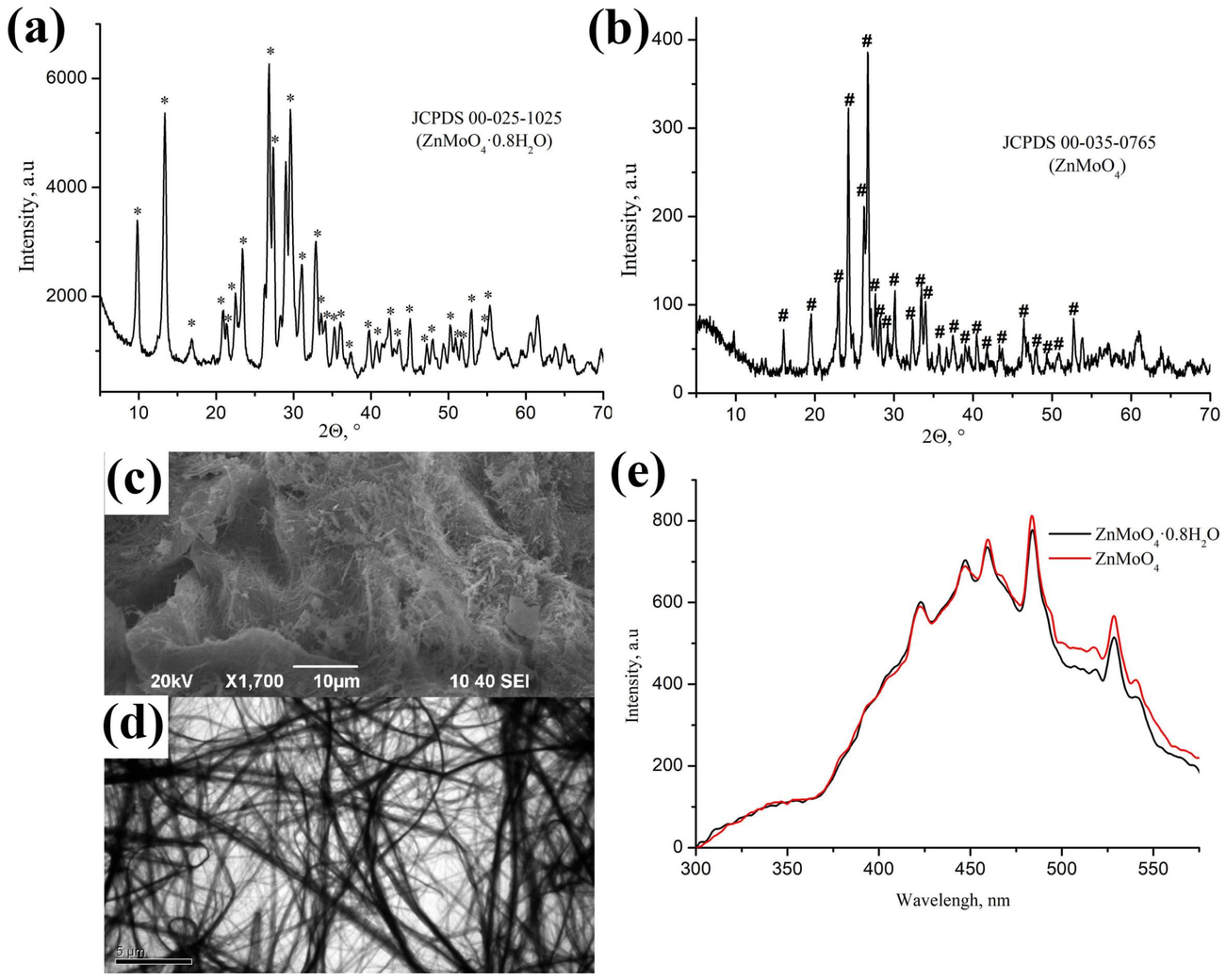

Fig.3. XRD data of (a) $ZnMoO_4 \cdot 0.8H_2O$ and (b) $ZnMoO_4$, (c) SEM image of $ZnMoO_4$ that obtained by 10 min MCh treatment, (d) TEM image of $ZnMoO_4 \cdot 0.8H_2O$ and (e) PL spectrum of $ZnMoO_4 \cdot 0.8H_2O$ and $ZnMoO_4$

Previously, it was shown that the MCh treatment of oxides in the planetary ball mill for 60 min in air does not lead to the formation of salts [2]. The data of X-ray diffraction showed that the treatment of oxides in an aqueous medium for 10 minutes leads to the formation of the $ZnMoO_4 \cdot 0.8H_2O$ phase without any impurities (Fig. 3 (a)). After calcinations at 300°C the crystalline water was removed and $ZnMoO_4$ phase was formed (Fig. 3 (b)). SEM and TEM (Fig. 3 (c,d)) methods show the formation of $ZnMoO_4 \cdot 0.8H_2O$ agglomerates from intertwining long nano-filamentary structures. After the removal of crystalline water long nano-filamentary structures was destroyed with the simultaneous formation of short rod structures. EDX analysis didn't show a uniform distribution of elements for samples after 10 min of MCh treatment. So, after 10 minutes of treatment a small amount of the initial oxides had not yet reacted. However, an increase MCh treatment time to 60 minutes leads to a uniform distribution of elements in the samples.

The PL specta of $ZnMoO_4 \cdot 0.8H_2O$ and $ZnMoO_4$ are shown in Fig.3 (e). PL spectra were measured at 280 nm excitation. Zinc molybdate exhibited photoluminescent emission in wide range (300-600 nm) with a maximum at 460 nm. It should be noted that the presence of crystalline water does not affect the intensity of the PL spectra.

Conclusions

Mechanochemical treatment makes it possible to carry out low temperature synthesis of salt from poorly soluble oxides as initial row materials. This new fast eco-friendly synthesis makes possible to obtained zinc molybdate with unique nano-filamentary structure. Zinc molybdate showed photoluminescent emission in range of 300 to 600 nm. It is shown that the phosphor properties of zinc molybdate do not depend on the presence of water in its structure.

[1] O. A. Diyuk and all Springer Proceedings in Physics. – 2021 – Vol. 263. P. 87-101 DOI 10.1007/978-3-030-74741-1_6

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