CHARACTERIZATION AND OPTICAL PROPERTIES OF MECHANOCHEMICALLY SYNTHESIZED $ZnMoO_4$

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INTRODUCTION

Recently, $ZnMoO_4$ find out many applications in science and technological field as red/green phosphors for light-emitting diodes, photocatalysts, scintillators, electrodes, sensors [1-5]. This compound crystallization in both forms: α-triclinic and β-monoclinic type structure. The main difference between them is the coordination of Mo ions which influence of the properties of this material. The Mo6+ ions are present in octahedral sites in the β polymorph and at tetrahedral positions in the α ones. The Zn-ions are in octahedral coordination in both forms. The α-triclinic form is the thermal stable phase at ambient conditions, while the β-phase is metastable and it was obtained mainly by hydrothermal route. The type of crystal phase obtained depends on the conditions of synthesis like precursors, time and temperature. The variety of methods for preparation of $ZnMoO_4$ have been applied as a solid-state reaction [6], sonochemical method [7], hydrothermal route [2,8]. Up to now mechanochemical treatment do not using for the obtaining of this phase. The many factors as milling speed, time of activation, diameter of balls, balls to powder weight ratio influence on the mechanochemical synthesis. Our previous investigations were shown that this approach led to direct synthesis of inorganic oxides [9-11]. The aim of the present work is to investigate the possibility for preparation of $ZnMoO_4$ by mechanochemically activation and to study its optical properties.

EXPERIMENTAL

$ZnO:MoO_3$ (1:1) BPR is 10:1

850 rpm/milling time

0h 5h 10h

Fritsch–Premium line–Pulversette No 7.

CHARACTERIZATION

- **Powder X-ray diffraction analysis (XRD)**-Bruker D8 advance diffractometer, using Cu-Ka radiation in the 2Θ range 10–80°; The average crystallite size was determined by the Scherrer's formula at diffraction peak 2Θ = 30.80 °.
- **Infrared spectroscopy (IR)**-Nicolet-320 FTIR spectrometer using the KBr pellet technique in range 1200-400 cm^{-1};
- **DR-UV-vis spectroscopy -**Evolution 300 UV-vis Spectrophotometer in range 200-1000nm; The optical band gap (Eg) was estimated from Tauc's equation: $(ahυ)^n = A(hυ - Eg)$, where, α – is the absorbance, *h* is Planck's constant, ν is the frequency, Eg is the optical band gap and *n* is ½ for indirect transition.
- **PL spectroscopy-**Horiba Fluorolog 3-22 TCS spectrophotometer equipped with a 450 W Xenon Lamp as the excitation source.

RESULTS AND DISCUSSION

The phase formation of $ZnMoO_4$ was monitored using XRD and IR analysis (Figs. 1 and 2). The early ball milling induced to the partially amourpization of MoO_3, only (Fig. 1). The new diffraction lines typical for metastable monoclinic $ZnMoO_4$ (PDF-00-025-1024) were observed after 3h milling time. The single phase was formed after 5h milling time at room temperature. The additional mechano-chemical activation up to 10 h did not lead to a significant change in the XRD pattern, which is an indication of the structural stability of $ZnMoO_4$. In the IR spectrum of the mechanochemically synthesized $ZnMoO_4$ powders (5 and 10h milling time) show the bands at 910, 835, 660, 625, 520, 455 and 405 cm^{-1} typical to the vibrations the MoO_6 and ZnO_6 structural units building the crystal structure of monoclinic $ZnMoO_4$ [2,8]. Optical properties were investigated by UV-Vis and photoluminescence (PL) spectroscopy measurements. Tauc's plot was used to evaluate the optical band gap (Eg) and show in inset of Fig. 3. The absorption spectrum of $ZnMoO_4$ shows the band at 320 nm is ascribed of O (2p)→ Mo (5d) charge transfer in the MoO_6–octhaderal group [11]. The band gap is estimated to be 2.95 eV, which is in good agreement with the previous reports [2,8]. The room temperature luminescence properties of as prepared $ZnMoO_4$ sample were investigated. The broad emission peak is observed at 405nm which consistent with the optical band gap estimated by Tauc's plot. The calculated CIE coordinates and color purity, show that the color-coordinates of the mechanochemical synthesized $ZnMoO_4$ fall in the blue region (Fig. 4).

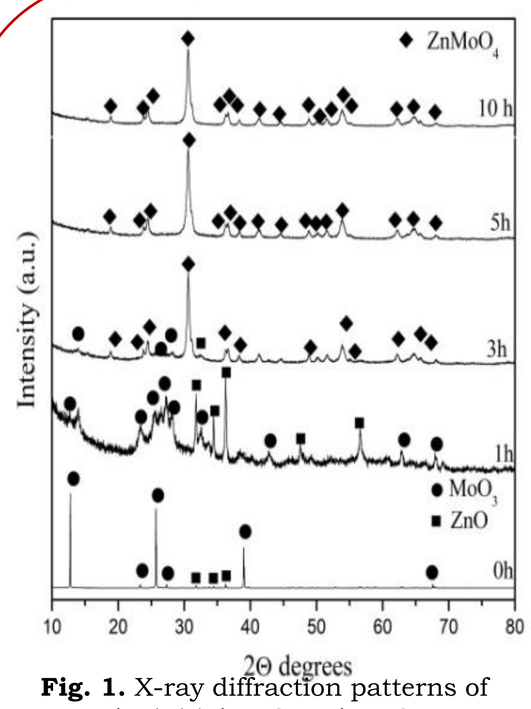

Fig. 1. X-ray diffraction patterns of the initial ZnO and MoO_3 mechanochemically activated for different milling times

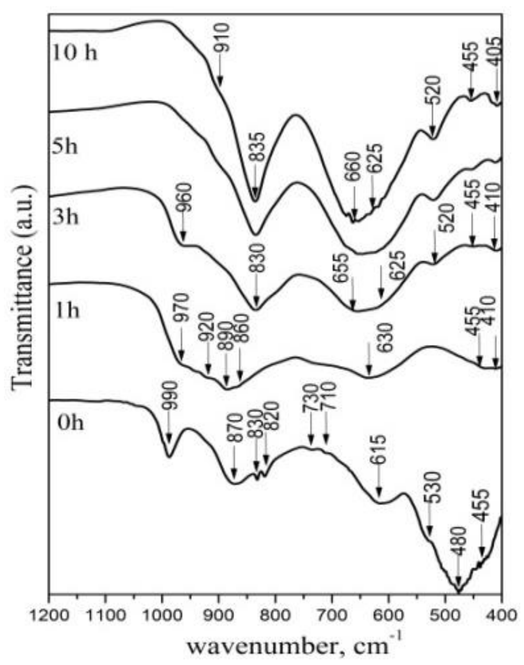

Fig. 2. IR spectra of the mixture of initial ZnO and MoO_3 mechanochemically activated for different milling times.

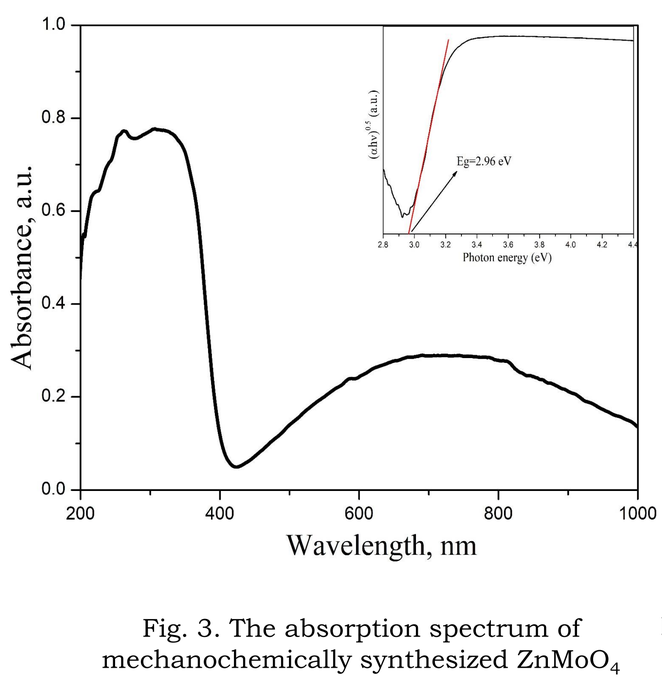

Fig. 3. The absorption spectrum of mechanochemically synthesized $ZnMoO_4$

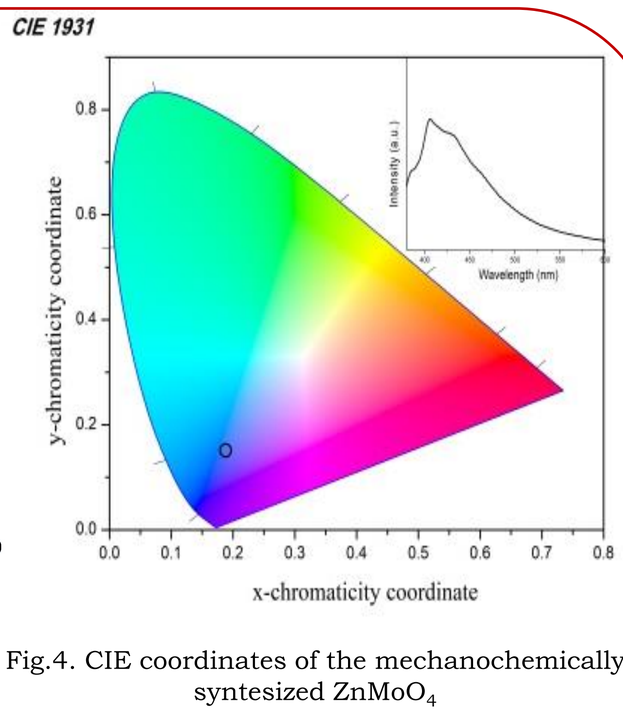

Fig.4. CIE coordinates of the mechanochemically syntesized $ZnMoO_4$

CONCLUSIONS

We established that mechanochemical treatment is a very appropriate method for the synthesis of zinc molybtate. It was found that 5 h milling of the reagents led to the complete crystallization of metastable β-$ZnMoO_4$ at room temperature. The prepared sample is indexed like single-phase of wolframite type structure with crystallite sizes of 30 nm and the optical band gap Eg=2.96 eV. From the PL emission spectra, the CIE parameters indicated that the as prepared $ZnMoO_4$ may be useful for lighting and display devices.

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