

## Nanosized $Zn_2SnO_4$ powders synthesized by coprecipitation and consecutive hydrothermal treatment in two different alkaline media

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A two-step method has been applied to the synthesis of zinc orthostannate,  $Zn_2SnO_4$ . As a first step X-ray amorphous hydroxide precursor had been obtained by coprecipitation of  $Zn(NO_3)_2$  and  $SnCl_2$  solutions using  $Na_2CO_3$ . In the second step the precursor was subjected to hydrothermal treatment (HT) in the presence of sodium hydroxide or ammonium hydroxide. The samples have been characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and UV-Vis spectroscopy. The precursor powder showed absorption edge at about 423 nm, while the absorption band of the HT samples, obtained in  $NH_4OH$  and  $NaOH$ , is shifted to 441 nm and 471 nm, respectively. The treatment of the amorphous precipitate in the presence of sodium hydroxide leads to a higher degree of crystallization, smaller sizes of the crystallites and higher photocatalytic activity for discoloration of the textile dye Methylene Blue (MB).

**Keywords:** zinc stannate, nanometer size, hydrothermal, photocatalyst, visible absorption

### INTRODUCTION

The zinc orthostannate  $Zn_2SnO_4$ , is a stable phase in the system  $ZnO-SnO_2$  having inverse spinel structure. Recently,  $Zn_2SnO_4$  has been intensively investigated with the view to its thermodynamic stability, high electrical conductivity, high electron mobility and low visible light absorption [1]. These properties of zinc orthostannate make it a suitable material with potential applications as anode in Li ion batteries [2], gas sensors [3, 4], in photoluminescence [5] and as photocatalysts [6].

However it is difficult to obtain  $Zn_2SnO_4$  by conventional solid state reaction. Hashemi et al. [7] have revealed that a single phase of zinc stannate is being formed during calcination at 1280°C for 12 h. Zinc ortho-stannate have been obtained by mechanical activation of the starting  $ZnO$  and  $SnO_2$  powders, followed by sintering at 1300°C, by Nikolic et al. [8]. The high temperature sintering at 1300 °C is undesirable and it be avoided by calcination of the co-precipitated with  $NaOH$  amorphous precursor of mixed zinc and tin hydroxides [9]. Another way to prepare zinc stannate at low temperature is the hydrothermal method. This method allows the obtaining of a homogeneous and well crystallized compound at much lower temperatures than the classical treatment. Therefore the deterioration of the properties as a result of undesirable sintering and

agglomeration processes is avoidable. Fang and et al. [10] have synthesized spinel  $Zn_2SnO_4$  via hydrothermal method at 220°C using aqueous solutions of  $Zn(CH_3COO)_2 \cdot 2H_2O$  and  $SnCl_4 \cdot 5H_2O$  and  $NaOH$  solution serving as mineralizer. Also, nanosized  $Zn_2SnO_4$  has been synthesized by the hydrothermal process in water/ethylene glycol mixed solutions [11].

Recently we have carried out coprecipitation of Zn and Sn hydroxides with  $Na_2CO_3$  from an aqueous solution mixture of  $Zn(NO_3)_2$  and  $SnCl_2$  and subsequent mechanical activation in order to prepare nanosized zinc stannate [12]. The advantage of sodium carbonate as precipitating agent is that the decomposition of the precursor is complete at lower temperatures (about 350°C).

Recently it has been demonstrated that  $Zn_2SnO_4$  exhibits high activities and durabilities for photodegradation of water soluble textile dyes [11, 13]. The methylene blue (MB), a typical textile dye, has been used as the model water pollutant to evaluate the photocatalytic activity of the hydrothermally prepared zinc stannate spinel powders.

To our best knowledge there are no available data on the preparation of  $Zn_2SnO_4$  powders by hydrothermal treatment of co-precipitate in basic media.

In this paper we are prepared crystalline  $Zn_2SnO_4$  powders by a two - step procedure: coprecipitation with  $Na_2CO_3$  of hydroxide precursor and consecutive hydrothermal treatment of the

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V. Blaskov et al.: Nanosized  $Zn_2SnO_4$  powders synthesized by co-precipitation and consecutive hydrothermal treatment. precipitate in different basic media (NaOH and  $NH_4OH$ ). Also the effect of the nature of basic media on the particles structure, morphology and activity in discoloration of textile dye as model waste water contaminant over the zinc stannate samples.

## EXPERIMENTAL

Aqueous solutions of 0.5 mol/l  $Zn(NO_3)_2 \cdot 6H_2O$  and 0.3 mol/l  $SnCl_2 \cdot 2H_2O$  (acidified to avoid hydrolysis) were prepared. The two solutions were mixed at component ratio corresponding to the stoichiometric molar ratio between the oxides participating in the  $Zn_2SnO_4$  ( $ZnO : SnO_2 = 2:1$ ). Sodium carbonate solution was used as a precipitating agent. In order to obtain a homogeneous precipitate, the sodium carbonate solution (0.5 mol/l) was added drop-wise, under intensive stirring. The final pH of the solution was 7.5. The obtained precipitate was being aged for 4 h, and then it was washed several times to until negative reaction for chloride ( $Cl^-$ ) anions was achieved. After that the precipitate was dried 12 h at  $60^\circ C$ . Two samples of precursor material, prepared by co-precipitation, were treated hydrothermally (HT) in basic media. Two samples of 1.5 g from the precursor material were treated hydrothermally 24 h at  $200^\circ C$  in 15 mL of 0.4 mol/l solution of NaOH or in 25 % wt.  $NH_4OH$ . The samples were filtered, then washed with distilled water and dried at  $100^\circ C$ .

The phase composition of the samples obtained was studied by X-ray diffraction (XRD) on Dron 3M diffractometer with  $CoK_\alpha$  radiation, applying accelerating voltage and current intensity of 40 kV and 40 mA respectively. The scan step was 0.02 degrees and acquisition time on each step was 1 second. The crystalline sizes of the samples were calculated based on X-ray peak profile broadening by using analysis program that applies Debye-Scherrer's equation. The particle morphology of the samples was observed by scanning electron microscope (SEM) JEOL-5510 at 10 kV accelerating voltage. The DR UV-Vis spectra were recorded on a Thermo Evolution 300 UV-Vis, equipped with a Praying Mantis device.  $BaSO_4$  is applied as a reference sample. The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG Escalab II electron spectrometer using  $AlK_\alpha$  radiation with energy of 1486.6 eV under base pressure  $10^{-7}$  Pa and a total instrumental resolution 1eV. The binding energies (BE) were determined utilizing the C1s line (from an adventitious carbon) as a reference with energy of 285.0 eV. The accuracy of measuring the BE values was 0.2 eV.

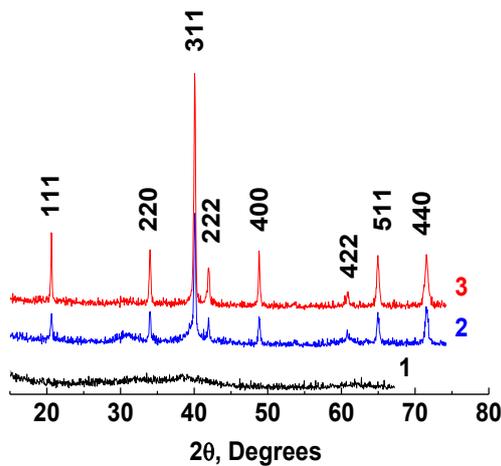
The photocatalytic activities of the samples were measured using an UV lamp with light intensity of  $5.10^{-5}$  W/cm<sup>2</sup>, located in the centre of the reactor. The latter contained aqueous solution (5 ppm) of Methylene Blue (MB) dye. This solution was homogenized with a magnetic stirrer at 400 rpm. The photocatalytic activity was evaluated by measuring the residual dye concentration at regular time intervals using Jenway 6400 spectrophotometer. The actual dye concentration was calculated by comparing the absorbance of the collected sample, measured at the wavelength of spectral maximum of the MB, based on calibration curve.

## RESULTS AND DISCUSSION

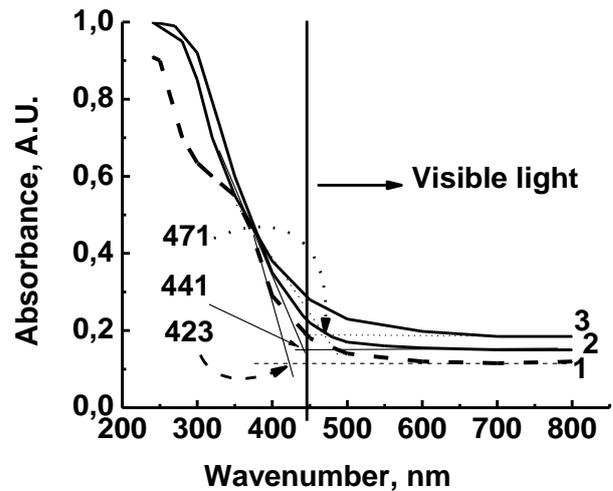
The X-ray diffraction patterns revealed that the starting precursor material, having  $Zn_2SnO_4$  composition, is X-ray amorphous, while both hydrothermally treated (HT) samples are crystalline (Fig.1). The crystalline sizes of the samples are calculated by the Debye-Scherrer's equation. The HT sample, prepared in the presence of NaOH, showed higher degree of crystallization and smaller crystallites size (25 nm) than that of the sample, prepared in the presence of  $NH_4OH$  (39 nm). The advantage of the two-step synthesis procedure (consisting of precipitation with  $Na_2CO_3$  and consecutive hydrothermal treatment) is the formation of nano-sized crystallites (24-70 nm) of zinc stannate. The conventional sintering process leads to bigger size of the crystallites of zinc stannate with dimensions higher than 100 nm [8].

Figure 2 represents the UV-Vis spectra of  $Zn_2SnO_4$  precursor powder and HT prepared samples.

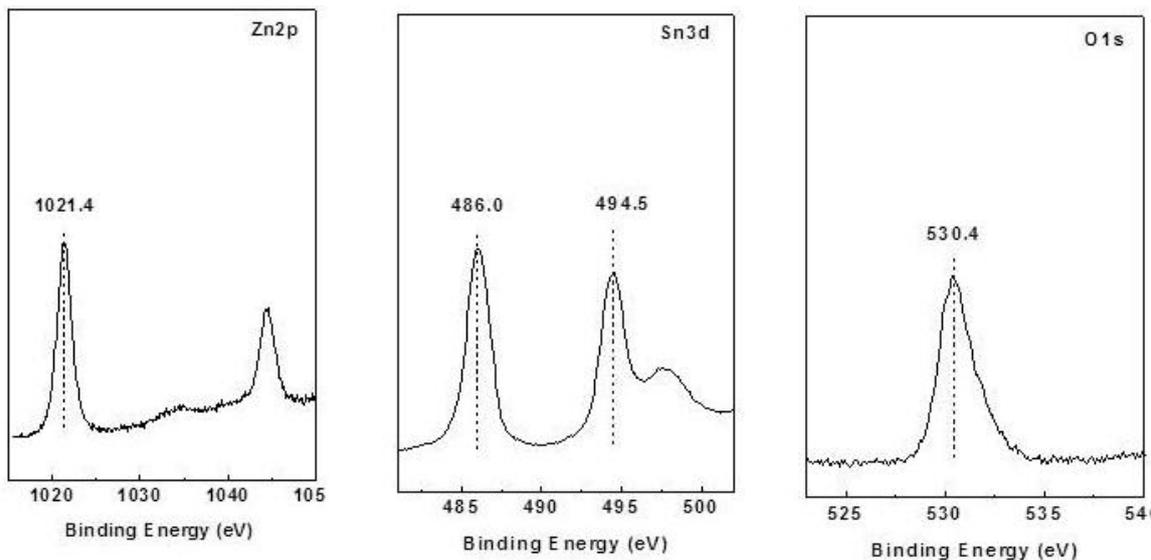
The UV-Vis spectra show red-shifting of the absorption band edge for the samples prepared in the presence of  $NH_4OH$  and NaOH respectively (Fig. 2), comparing with the precursor material. The vertical line at about 450 nm in Fig. 2 schematically represents the value of the end of ultraviolet part and the beginning of the blue part of the visible spectra. The precursor powder showed absorption band edge at about 423 nm, which is shifted to 441 nm and 471 nm for the hydrothermally prepared zinc stannate in the presence of  $NH_4OH$  and NaOH, respectively. The shift in the absorption band edge to the visible part of spectra proved that the hydrothermal treatment in basic media of precipitated amorphous  $Zn_2SnO_4$  is a promising method for the preparation of photocatalysts, potentially active under solar light irradiation.



**Fig.1.** XRD patterns of the samples. 1-precursor material, 2 - HT prepared in the presence of  $NH_4OH$ , 3 – HT prepared in the presence of  $NaOH$ . For a better observation, the X-ray patterns are shifted upwards.



**Fig.2.** UV-Vis spectra of starting precursor - 1, and HT prepared samples in the presence of  $NH_4OH$  - 2 and in the presence of  $NaOH$  - 3. The values of absorption band edges are indicated.



**Fig.3.**  $Zn2p$  (a),  $Sn3d$  (b) and  $O1s$  (c) core level XPS spectra of HT-  $Zn_2SnO_4$  in  $NH_4OH$ .

The XPS spectra of the samples are shown in Fig. 3. The characteristic peak of  $Zn2p_{3/2}$  is located at 1021.4 eV, which is typical of  $ZnO$  (Fig 3). The binding energies of  $Sn 3d_{5/2}$  and  $Sn 3d_{3/2}$  core electrons are located at 486.0 and 494.5 eV, respectively. The position of the  $O1s$  peak at 530.4 eV corresponds to the state of the oxygen atom  $O^{2-}$  in the zinc stannate. The XPS spectra of the sample, prepared in the presence of  $NH_4OH$ , did not display  $N1s$  peak at binding energy of about 399.8 eV, showing that nitrogen is not incorporated in the sample during the hydrothermal treatment.

The SEM micrographs of the hydrothermally treated powders are shown in Fig. 4. The general morphology of HT synthesized products consists of aggregates, which are not distinguishable from one another. The size of the particles depends on the type of the basic media. It has to be noted that the samples treated in  $NH_4OH$  possess large aggregates with non-uniform sub-micron and micron-sized particles (Fig. 4a), while in  $NaOH$  the aggregates are smaller. Thus the treatment in  $NaOH$  leads to the formation of smaller particles with size within the range 100 - 300 nm (Fig. 4b).

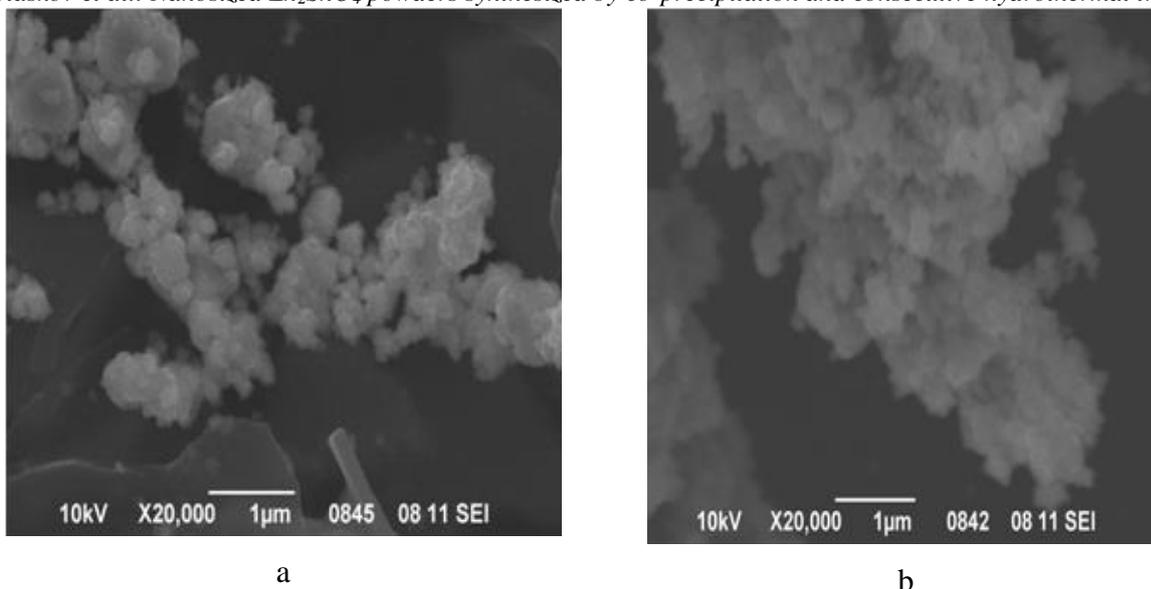


Fig.4. SEM micrographs of  $Zn_2SnO_4$  powders HT treated in  $NH_4OH$  (a) and  $NaOH$  (b)

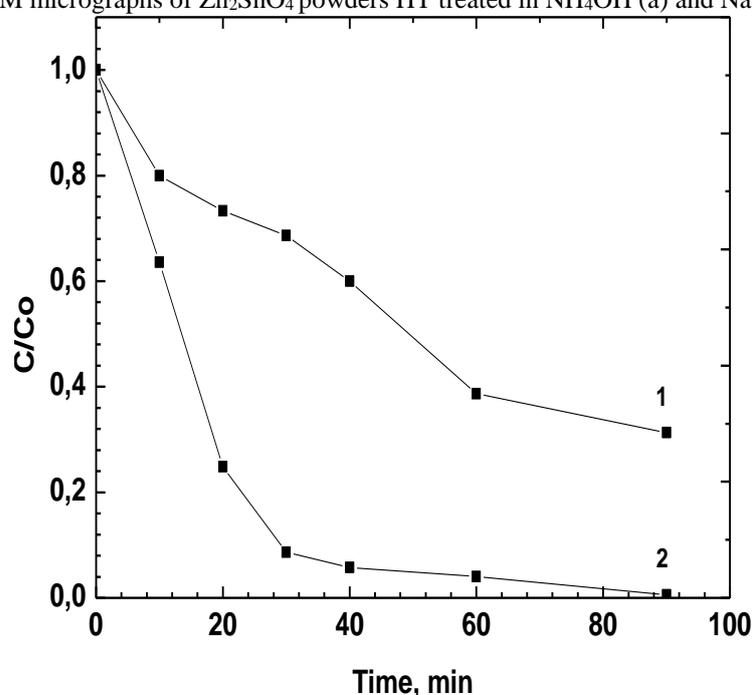


Fig.5. Photocatalytic discoloration of MB by  $Zn_2SnO_4$ -HT prepared in the presence of  $NH_4OH$  (1) and  $NaOH$  (2).

The photocatalytic activity of  $Zn_2SnO_4$  powder was followed based on the change in the relative concentration  $C/C_0$  (where  $C_0$  is initial concentration of MB dye) with the time under UV illumination (Fig. 5). When the  $Zn_2SnO_4$  is being irradiated, electrons in the valence band (VB) are being excited to the conduction band (CB). Simultaneously holes are being generated in the VB, which are reacting immediately with the dye or interacting with the surface-bound  $H_2O$  or  $OH$  to produce the  $OH^\cdot$  radical species – a strong oxidant for the mineralization of MB. Generally, the overall photocatalytic activity of semiconductors is primarily depending on its adsorption capacity, on

the specific surface area, the structure and morphology. Therefore the high photocatalytic activity of the nanocrystalline  $Zn_2SnO_4$  could be attributed to the smaller crystallites size and respectively to the higher specific surface area, which is more favorable for the mass transfer reactions in the liquid phase. Another factor influencing the activity is the particles aggregates [14]. The size and distribution of particle aggregates in the samples obviously influence the light absorption and light scattering, which are determining the degree of photon interaction with the catalyst surface. The intensity of the light scattered from the surface of ammonia treated

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### CONCLUSIONS

Nano-sized  $Zn_2SnO_4$  powders have been obtained by two-step synthesis procedure, consisting of co-precipitation of mixed zinc stannate - amorphous hydroxi-carbonates and their consecutive hydrothermal treatment in basic media (NaOH or  $NH_4OH$ ). The samples, prepared in NaOH, showed higher degree of crystallinity and smaller size crystallites, than those of the powders, prepared in the presence of  $NH_4OH$ . The photocatalytic activity in methylene blue discoloration of  $Zn_2SnO_4$ , hydrothermally prepared in the presence of NaOH, reaches almost 90% degradation degree of the dye within 30 min under UV irradiation. Both HT samples showed red shift in the UV-Vis spectra. The samples prepared by this two-step synthesis method showed absorption at visible wavelengths, which proves that they are promising materials for the preparation of photocatalysts active under visible light.

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## НАНО-РАЗМЕРНИ ПРАХОВЕ ОТ $Zn_2SnO_4$ , СИНТЕЗИРАНИ ЧРЕЗ СЪ-УТАЯВАНЕ И ПОСЛЕДОВАТЕЛНО ХИДРОТЕРМИЧНО ТРЕТИРАНЕ В ДВЕ РАЗЛИЧНИ АЛКАЛНИ СРЕДИ

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(Резюме)

Цинковият ортостанат  $Zn_2SnO_4$  беше получен посредством двустадийен метод. Първоначално беше синтезиран рентгеноаморфен хидроксид чрез съутаяване от разтвори на  $Zn(NO_3)_2$  и  $SnCl_2$  и утайтел  $Na_2CO_3$ . На втория стадий полученият прекурсор беше обработен хидротермално (ХТ) в среда на натриев хидроксид или амониев хидроксид. Така получените образци бяха охарактеризирани чрез ренгенофазов анализ (РФА), ренгенова фотоелектронна спектроскопия (РФС), сканираща електронна микроскопия (СЕМ) и UV-Vis спектроскопия. За прахообразния изходен образец беше регистриран абсорбционен ръб при 423 nm, докато при образците, получени хидротермално ХТ в среда от  $NH_4OH$  и NaOH той се измества съответно към 441 nm и 471 nm. Обработката на аморфната утайка в среда на натриев хидроксид води до по-добра кристализация, по-малки размери на кристалитите и по-висока фотокаталитична активност при окислително обезцветяването на текстилното багрило метиленово синьо (МВ).

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