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Mechanochemical synthesis and photocatalytic properties of zinc titanates ♦

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A mixture consisting of both cubic $ZnTiO_3$ and Zn_2TiO_4 was synthesized by ball milling at room temperature. A stoichiometric mixture of nano ZnO and TiO_2 powders in a 1:1 molar ratio was subjected to intense mechanical treatment in air using a planetary ball mill (Fritsch – Premium line – Pulverisette No. 7) for a period from 5 to 120 min. The phase formation and the structural transformation were followed by X-ray phase analysis and IR spectroscopy. The synthesis of the zinc titanates started after 30 min and finished after 45 min milling time at a high speed (1000 rpm). The agglomeration tendency and the crystal size of the obtained powders were determined by scanning electron microscopy. The photocatalytic activity of the samples was investigated by degradation of a model aqueous solution of malachite green (MG) upon UV-irradiation.

Key words: $ZnTiO_3$, mechanochemical activation, photocatalytic properties.

INTRODUCTION

Zinc titanates are attractive materials owing to their various applications as paints, pigments, thermistors, sorbents, microwave dielectrics, dielectric resonators, catalysts, etc. [1-6]. Several compounds are known to exist in the ZnO-TiO_2 system: Zn_2TiO_4 congruently melting above 1500^0C; $ZnTiO_3$ stable up to 945^0C and $Zn_2Ti_3O_8$ which was found later [1, 7]. Both zinc titanates ($ZnTiO_3$ and Zn_2TiO_4) are electroceramic materials with interesting dielectrical properties and low sintering temperatures [8, 9]. There are several methods for preparing $ZnTiO_3$ powders, generally focused on conventional solid state reactions [1, 10], mechanochemical activation [11, 12], precipitation [13, 14] and several variants of the sol-gel technique [1, 10, 15-18]. The attempts to synthesize pure $ZnTiO_3$ by thermal treatment of ZnO/TiO_2 mixtures are generally unsuccessful because this titanate decomposes at high temperatures (~950^0C). According to the review analysis, up to now $ZnTiO_3$ phase was always obtained simultaneously with Zn_2TiO_4 using the mechanochemical activation method [11, 12]. High energy ball milling was applied on the ZnO-TiO_2 system in order to obtain the most stable Zn_2TiO_4 phase [19-21]. It was established that intensive milling conditions favor the formation of low temperature titanate forms. Very recently, Labus *et al.* [12] established coexistence of $ZnTiO_3$, Zn_2TiO_4 and TiO_2 (rutile) in a low temperature region below 945^0C for the composition with stoichiometric ratio 1:1. Generally, the mechanochemical activation of crystalline solids performed in high-energy mills becomes a very useful method to control the reactivity in the solid state [22]. Moreover, the milling conditions were limited up to 400-500 rpm, which did not exhaust the possibilities for synthesis by this method. Up to now the influence of the dispersity of the used precursors was not studied in the literature. For this reason, the study of new routes of synthesis of zinc titanates needs to be explored. That is why we were motivated to continue the investigations in the binary system ZnO-TiO_2 using high energy ball milling in order to control the process of synthesis.

The purpose of the present work was to study and to verify the behavior of the ZnO-TiO_2 system under new experimental conditions of mechanochemical activation of nano oxides (ZnO, <100 nm and TiO_2, < 25 nm) in order to obtain zinc titanates.

EXPERIMENTAL PROCEDURE

Nanopowders of zinc oxide (Sigma-Aldrich,

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<100 nm) and titanium oxide (anatase) (Sigma-Aldrich, < 25 nm) were used as starting materials.

The initial mixture of ZnO and TiO_2 in a molar ratio 1:1 was subjected to intensive mechanochemical activation in a planetary ball mill (Fritsch–Premium line–Pulverisette 7). The milling speed was 1000 rpm. Stainless steel vials and balls of 5 mm diameter were used. The balls:powder weight ratio was 10:1 and the milling time - from 5 to 60 min.

The phase and structural transformations were monitored by X-ray diffraction (XRD) and infrared (IR) spectroscopy. Powder XRD patterns were registered with a Bruker D8 Advance diffractometer using Cu Kα radiation in the range from 10 to 80^0. The thermal behavior of the powders was examined by differential thermal analysis (LABSYS^{TM} EVO apparatus). Infrared spectra were registered in the range 1200-400 cm^{-1} on a Nicolet-320 FTIR spectrometer using the KBr pellet technique. Morphologies and crystallite sizes of the obtained samples were characterized by scanning electron microscopy (JEOL Superprobe 733). The photocatalytic activity of the powder was studied using malachite green (MG) (Sigma-Aldrich) dye after subjecting it to UV-radiation. The UV irradiation was carryed out using an UV-lamp (Sylvania BLB, 18 W, λ ~ 315–400 nm). The aqueous solution of MG (150 mL, 5 ppm) containing 0.1 g of the prepared powder was placed in a vessel. Before photodegradation, an adsorption-desorption equilibrium state was established by ultrasonic and mechanical stirring for 10 min. Volumes of 3 mL were taken from the solution at given time intervals and separated through centrifugation (5000 rpm, 5 min). Then the concentration of MG in the solution was determined with a Jenway 6400 spectrophotometer.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the samples obtained are presented in Fig. 1. The diffraction lines of the obtained products $ZnTiO_3$ and Zn_2TiO_4 were indexed using JCPDS database. The interaction between the initial oxides started after 15 min and completed after 45 min milling time. On the diffractogram pattern for the milling time of 30 min, reflection characteristics for both cubic $ZnTiO_3$ (JCPDS 39-0190) and Zn_2TiO_4 (JCPDS 77-scanning electron microscopy (JEOL Superprobe 733). The photocatalytic activity of the powder was 0014) occurred. It is seen that after 15 min a small amount of $FeTiO_3$ (JCPDS 75-0519) appeared in the X-ray diffraction pattern. The prolongation of the mechanochemical treatment up to 120 min at the same milling speed did not lead to a change in the XRD patterns of the samples. Obviously, this high milling speed is decisive for the rapid synthesis. The presence of TiO_2 (rutile) was not established in our study in contrast to Labus *et al*. [12], which did not achieve a complete synthesis.

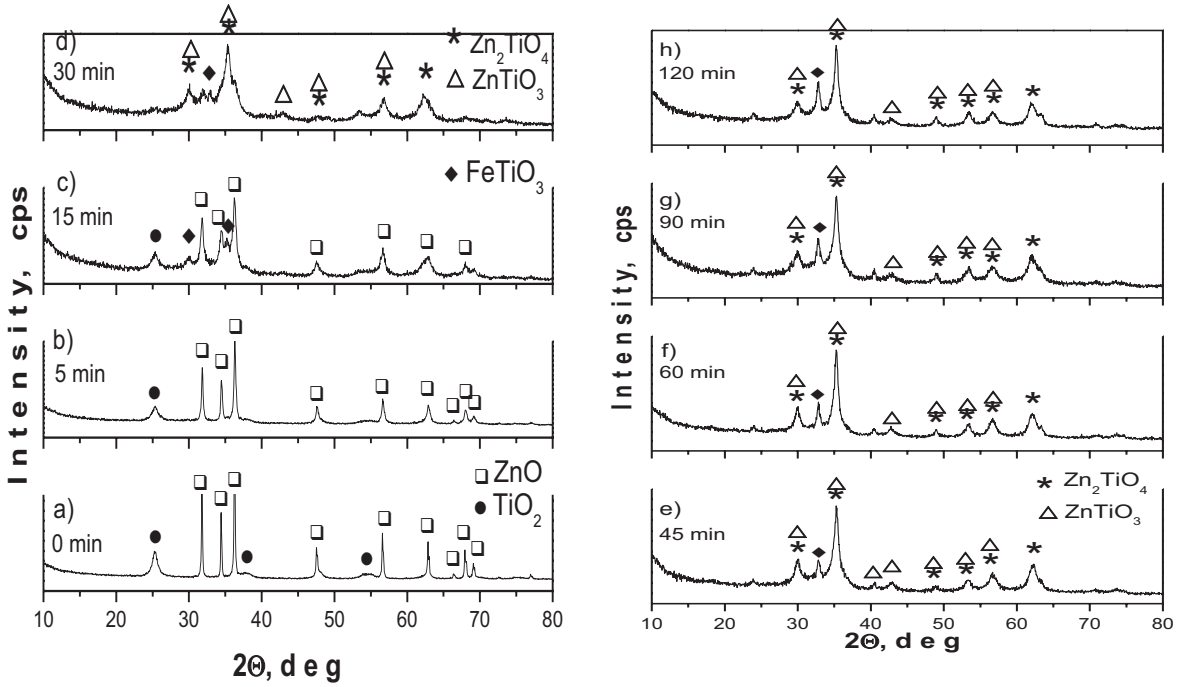

Fig. 1. XRD patterns of the mixture at different milling time

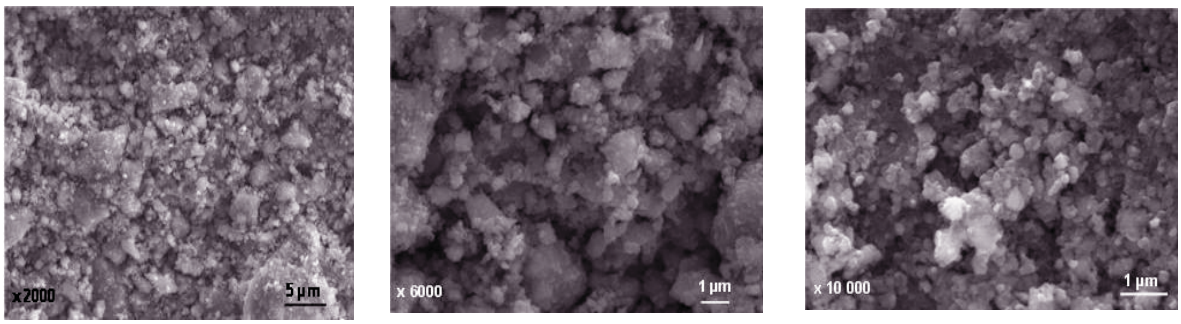

Fig. 2. SEM images of the obtained powders after 60 min milling time at different magnifications.

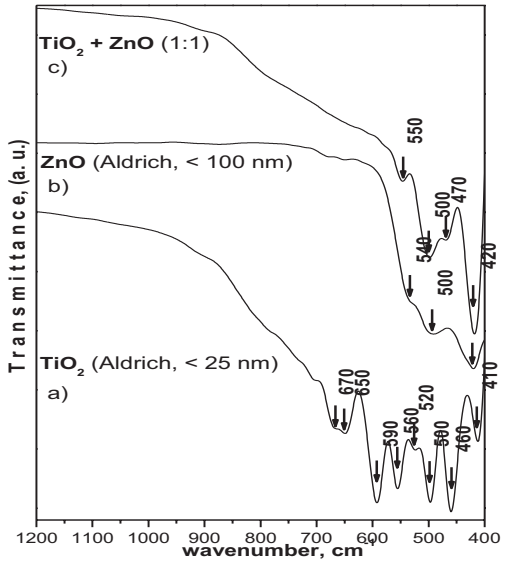

Fig. 3. IR spectra of the mixture at different milling time

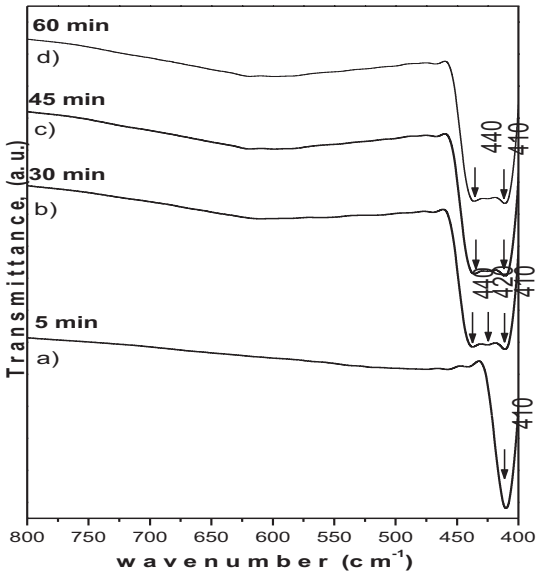

Fig. 4. IR spectra of TiO_2, ZnO and mixture of ZnO and TiO_2

Our results differ from those in the literature owing to the higher activity of the powders and the more intensive mechanochemical activation. Thereby, the selected experimental conditions in this study provided completeness of the zinc titanates synthesis. For comparison, similar results were obtained by Labus *et al*. [12] after 80 min milling time and by Qian *et al*. [23] – after 10 hours milling time. The average crystalline size of the obtained powders calculated from the broadening of the diffraction line using Sherrer's equation is about 60-70 nm. The morphology and particle size of the powders obtained after 60 min milling time are presented in Fig. 2. The SEM results showed that the obtained product consisted of agglomerates with average size below 1 μm.

IR spectroscopy was used to confirm the synthesis of the crystalline material. The absorption bands of the pure oxides TiO_2 (bands at 670, 650, 590-480 and 410 cm^{-1}) and of ZnO (bands at 540, 500 and 420 cm^{-1}) are shown in Fig. 3, while Fig. 4 presents the IR spectra of the mixtures after different milling times. As it is seen the IR spectrum of the mixture after 5 min milling time is different from the IR spectrum of the mixture without mechanochemical activation because the bands corresponding to TiO_2 disappeared (Fig. 3c). One band only, at 410 cm^{-1}, is observed that could be assigned to the vibration of ZnO polyhedra [24-26] and this may be an indication of the beginning of the chemical reaction (Fig. 4). It is well known that the bands corresponding to ZnO_n polyhedra are in this absorption range. This peculiarity was not found in the X-ray diffraction patterns, where the diffraction lines of the starting materials were found, but the strongest peak of TiO_2 decreased (Fig. 1b). At 30 min milling time new bands appeared in the same spectral range (about 440 and 420 cm^{-1}) which pointed to the continuation of the synthesis. Between 30 min and 45 min milling time the IR spectra changed which could be related to the synthesis of crystalline phases. According to

some authors [1, 27], the appearance of the bands about 450-440 cm^{-1} could be related to the Ti-O stretching vibrations in $ZnTiO_3$.

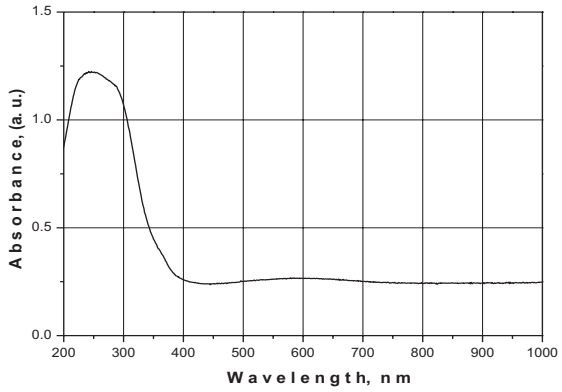

Fig. 5.UV-VIS spectrum of $ZnTiO_3$ powder obtained by mechanochemical activation

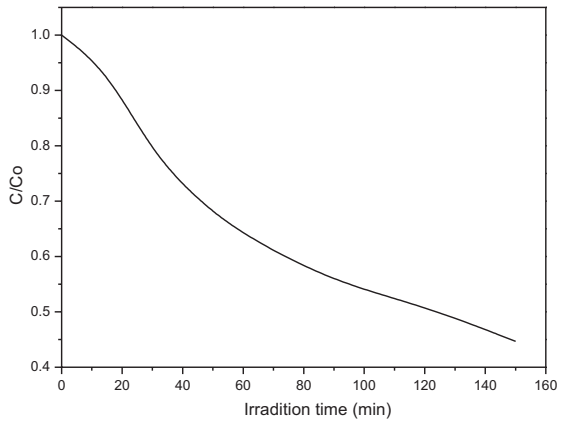

Fig. 6. Photocatalytic degradation of Malachite Green (MG) by $ZnTiO_3$ powder

The UV-Vis spectrum of the sample obtained after 60 min milling time is shown in Fig. 5. As it is seen the obtained powder is highly transparent in the visible region. The UV-Vis spectrum shows that the absorption edge starts at about 240 nm. Fig. 6 shows the temporal evolution of the concentration (C/C_0) of MG, where C_0 and C represent the initial equilibrium concentration and the reaction concentration of MG, respectively. The photodegradation of MG was completed in 150 min and it was compatible to the photocatalytic activity of ZnO and TiO_2 [26, 28] (Fig. 6).

CONCLUSIONS

A mixture of both cubic $ZnTiO_3$ and Zn_2TiO_4 was successfully prepared under new experimental conditions: 45 min milling time and milling speed of 1000 rpm. The mechanochemically obtained mixture of zinc titanates displays photocatalytic activity towards the degradation of malachite green after 150 min irradiation time. The UV-Vis spectrum shows that the obtained sample is transparent in the visible range of the spectrum.

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МЕХАНОХИМИЧЕН СИНТЕЗ И ФОТОКАТАЛИТИЧНИ СВОЙСТВА НА ЦИНКОВИ ТИТАНАТИ

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(Резюме)

Смес, съдържаща кубичните форми на $ZnTiO_3$ и Zn_2TiO_4, е синтезирана по механохимичен път при стайна температура. Стехиометричната смес, съдържаща нано ZnO и TiO_2 прахове в моларно съотношение 1:1, е подложена на интензивна механична обработка на въздух в планетарна топкова мелница (Fritsch – Premium line – Pulverisette No. 7) за период от 5 до 120 мин. Фазообразуването и структурните трансформации са проследени чрез рентгенофазов анализ и ИЧ спектроскопия. Установено е, че синтезът на цинковите титанати започва след 30 мин и приключва след 45 мин механохимично третиране при висока скорост (1000 оборота). Тенденцията за агломериране и размерът на получените прахове са определени чрез СЕМ. Фотокаталитичната активност на образците е изследвана чрез разлагането на моделен разтвор на малахитово зелено (MG) под влияние на УВ лъчение.