Research Article

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Mechanochemical synthesis of zincite doped with cadmium in various amounts

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Abstract: This work investigates the limit of Cd doping in ZnO derived by means of mechanochemical synthesis using CdCl_2 , ZnCl_2 and Na_2CO_3 as precursors and NaCl as diluent. The prepared samples were characterized using X-ray diffraction (XRD), Fourier transformed infrared attenuated total reflectance (FTIR ATR) spectroscopy, UV-Vis diffuse reflectance spectroscopy (DRS), N_2 adsorption-desorption isotherms, scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS), while photocatalytic efficiency has been evaluated for methylene blue degradation process. Zn for Cd replacement limits in the crystal lattice of ZnO derived via mechanochemical synthesis were found to be only 2%. For Cd present in a larger portion, CdO and CdCO_3 phases appear. Cd doping limits in ZnO were not affected by the milling interval. However, it was observed that Cd doping impairs the nanocrystallinity of ZnO. The morphology and the electronic structure of ZnO and thus photocatalytic activity was inappreciably affected by the Cd doping.

Keywords: Cd doped ZnO, mechanochemical synthesis, methylene blue, photocatalyst, solid solution

1 Introduction

Zinc oxide or zincite, ZnO is a versatile material widely used for its catalytic, electrical, optoelectronic, and photochemical properties [1–3]. Due to its high catalytic activity, large surface area and long-term stability ZnO is a promising candidate for heterogeneous catalysis [4]. However, large ZnO band gap energy of 3.37 eV [5] and rapid recombination of photogenerated electrons and holes [6] hampers

its practical applications. Zincite doping with transition metals has been proven as an efficient technique of narrowing the band-gap and capturing photogenerated carriers at surface, thus expanding its spectral response to visible region and restraining recombination process and in such manner improving the photocatalytic activity of ZnO [7]. In order to modify zincite properties cadmium is frequently used [5]. Cadmium doped ZnO has been prepared by methods such as: combustion synthesis [8], thermolysis [9], spray pyrolysis [10], coprecipitation [4], sonochemical synthesis [7], hydrothermal [6], polyol method [11], sol-gel process [12], etc. These researches had different goals and in some cases the dopant share was as low as 1.2% [4]. However, in some articles, the reported cadmium content in zinc is as high as 40% [7]. Some of listed methods are complicated, difficult to control or require costly equipment or precursors. Some turned out inconvenient for obtaining nanocrystalline ZnO or caused high degree of agglomeration [13].

Mechanochemical synthesis is a simple and affordable technique for nanoparticles preparation. According to Acharya [14] the incorporation of Cd into ZnO over mechanochemical synthesis seem to be very useful for the fabrication of ZnO/ZnCdO heterojunction and superlattice structures, which are the key elements in ZnO based light emitters and detectors. In the course of mechanochemical synthesis the chemical transformation is induced by mechanical force [15]. The papers on mechanochemical synthesis of cadmium-doped zincite are rare. Salvi *et al.* [16] report on Cd and Sr co-doped ZnO prepared from metal acetate precursors and oxalic acid hand ground in agate mortar where Cd to Zn ratio was approximately 0.025:1. Vidyasagar *et al.* [17] used metal chlorides and sodium hydroxide as precursors and polyethylene glycol as a diluent and also carried out the reaction in agate mortar. Unfortunately, the authors fail to disclose the Cd to Zn ratio. Both papers report on successful implantation of cadmium ions in zincite crystal lattice and the consequent modifications of properties.

A systematic study on mechanochemical synthesis of cadmium-doped zincite could not be found to the best of our knowledge. In addition, for obtaining reliable data, preparation should be carried out utilizing equipment that

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enables a better control of the synthesis conditions. Therefore, a planetary mill was used in this investigation in attempt to utilize systematic mechanochemical synthesis of zincite doped with cadmium in various amounts. The doping limits of Cd incorporation in ZnO were studied by paying special care to the influence of Cd doping on the structure, morphology, properties and catalytic activity of ZnO.

2 Experimental

2.1 Synthesis

Mechanochemical synthesis was carried out using a Fritsch Pulverisette 6 planetary mill with 250 ml corundum bowl and 16 mm diameter corundum balls. Analytical reagent grade zinc chloride, ZnCl_2 (Kemika, Croatia), cadmium chloride, CdCl_2 (Kemika, Croatia) and sodium carbonate, Na_2CO_3 (Kemika, Croatia) were used as precursors while sodium chloride, NaCl (Kemika, Croatia) was used as a diluent in order to separate nanoparticles produced by reaction and prevent their subsequent growth. Before use precursors were dried at 105°C for 24 h in a laboratory drier.

Non-doped sample has been synthesized as follows: firstly, a 180 g of balls were placed in a bowl. Then a 0.05 mol (~ 6.85 g) of ZnCl_2 , a 0.05 mol (~ 5.30 g) of Na_2CO_3 and a 0.3 mol (17.52 g) of NaCl were weighted in a corundum bowl. Thus the molar ratio of precursors and diluent was $n(\text{NaCl}) : n(\text{ZnCl}_2) : n(\text{Na}_2\text{CO}_3) = 6 : 1 : 1$ while ball to powders weight ratio was $\sim 6 : 1$. Powders mixture was milled in a planetary mill for 2 h at 600 rpm in order to induce a solid state reaction resulting with the formation of ZnCO_3 . Resultant powder was transferred in corundum crucible and calcined in a box furnace at 600°C in static air for 2 h in order to decompose ZnCO_3 to ZnO. Calcined powder was washed with deionized water in order to remove NaCl which, besides being added as a diluent was also created as a reaction by-product. NaCl was removed by procedure consisted of mixing powder in deionized water in an ultrasonic bath. Insoluble ZnO has been separated from dissolved NaCl by centrifugation at 3000 rpm for 5 min. followed by decanting. Washing procedure was performed a total of six times. Finally, the resultant ZnO powder was dried at 105°C for 24 h in a laboratory drier.

Doped samples were synthesized in a same manner except that a part of ZnCl_2 is replaced with CdCl_2 in order to substitute a part of the zinc in zincite crystal lattice with cadmium. In such manner a series of samples with nominal formula $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ where x was 0, 0.01, 0.02, 0.03,

0.04 and 0.05 were prepared. Samples were denoted as ZCO ($x=0$), ZC1 ($x=0.01$), ZC2 ($x=0.02$), ZC3 ($x=0.03$), ZC4 ($x=0.04$) and ZC5 ($x=0.05$) and stored in a closed glass container.

2.2 Characterisation

The powder X-ray diffraction were obtained using Shimadzu diffractometer XRD 6000 with $\text{CuK}\alpha$ radiation. Data were collected in a step scan mode with steps of $0.02^\circ 2\theta$ and counting time of 0.6 s/step.

Calculation of lattice parameters were made by using UnitCell program [18], corundum introduced in the sample by mill and balls wearing has been used as internal standard.

The average crystallite size of samples was calculated out of the broadened (101) diffraction peak using Scherrer's equation [19]: $d = k\lambda / (\beta \cos \theta)$, where d is the average crystallite diameter, k is the Scherrer's constant (0.94), λ is the X-ray wavelength (0.15418 nm), β is the full width at half height of (101) diffraction peak corrected for instrumental broadening and θ is the diffraction angle.

IR spectra were acquired using the Bruker Vertex 70, Fourier transform infrared spectrometer set on attenuated total reflectance mode. The samples were pressed on a diamond and the absorbance data were collected between 400 and 4000 cm^{-1} with spectral resolution of 1 cm^{-1} and average of 64 scans.

The UV-Vis reflectance spectra of the prepared samples were obtained using DRS (Shimadzu UV-3101PC) equipped with an integrating sphere. BaSO_4 was used as a white reference. The measured spectra were transformed using Kubelka-Munk transformation: $F(R) = (1-R)^2 / (2R)$, where $F(R)$ is proportional to the extinction coefficient (α) and R is the reflectance [20]. The bandgap energy, E_g , was determined by plotting $(F(R)h\nu)^n$ vs. photon energy ($h\nu$), the so-called Tauc's plot, where h is Planck's constant (4.13566733 eVs), ν is frequency (quotient of light velocity ($c=299792458\text{ ms}^{-1}$) and wavelength (λ / m)) while n is the coefficient associated with electronic transition and for direct allowed transitions is equal to 2 [20]. Bandgap is obtained by extrapolation of the linear region of the $(F(R)h\nu)^n$ vs. $h\nu$ curve onto the energy axis.

The morphologies of the prepared powders were investigated with Tescan Vega 3 EasyProbe scanning electron microscope operating at 10 kV, additionally equipped with an EDS spectrometer Oxford INCA X-sight. Samples for SEM characterization were fixed on a sample holder using double-sided carbon conductive tape and then coated with gold using Quorum SC 7620 sputter coater.

Surface area was determined by Brunauer-Emmet-Teller (BET) N_2 gas adsorption-desorption isotherms obtained at 77 K on Micromeritics ASAP-2000 equipment. Samples were previously degassed at 100°C under dynamic vacuum of 1.3×10^{-2} Pa. Pore size distributions were calculated from the desorption isotherms by the Barret, Joyner, Halenda (BJH) model.

The photocatalytic activity of nanocrystalline zincite was determined by studying the degradation of methylene blue as a model compound. The photodegradation experiments were carried out at room temperature (25°C). A borosilicate cylindrical glass vessel with 100 mm diameter and 120 mm height was used as photocatalytic reactor. A quartz glass tube with a lamp inside was placed axially in the centre of the vessel. Pen Ray lamp (UVP Products Cat. No. 90-0012-01), with radiation wavelength 254 nm and emission intensity 2 mWcm^{-2} , was used as UV source. A 500 cm^3 of 14 ppm methylene blue aqueous solution containing 25 mg of catalyst was placed in a reactor. The mixture was stirred using magnetic stirrer operating at 300 rpm to maintain homogeneous reaction mixture and irradiated. Aliquots of 5 cm^3 were withdrawn from the mixture by a syringe. First aliquot was withdrawn from the mixture 30 min before the commencement of irradiation. After that, the aliquots were taken at regular intervals of 15 min. The photo-degradation was monitored with a UV-Vis Varian, Cary 1E spectrophotometer. Spectra were acquired and intensity of main methylene blue absorption band at $\sim 664 \text{ nm}$ measured. The degradation of a substance was depicted as discoloration ratio as a function of the irradiation time. The discoloration ratio was calculated as ratio between absorbance after measurement interval and absorbance of initial MB solution.

3 Results and discussion

Figure 1 shows the XRD pattern of non-doped sample as well as patterns of Cd-doped samples. All samples exhibit the presence of a phase with hexagonal wurtzite structure identified as **zincite**, ZnO (ICDD PDF No. 36-1451). All XRD patterns also display minor peaks due to corundum, Al_2O_3 (ICDD PDF No. 46-1212) which is inevitably present due to the wearing of the mill jar and balls.

In the non-doped sample and doped samples with 1 and 2% of Cd, the zincite is the sole phase, while samples doped with 3, 4 and 5% of Cd beside main zincite phase also show the presence of minor phase; **otavite**, CdCO_3 (ICDD PDF No. 42-1342). The appearance of Cd-bearing phase in sample doped with 3% of Cd points out to the

Figure 1: XRD patterns of mechanochemically prepared samples with various portions of dopant.

Figure 2: XRD patterns of samples with 5% of Cd milled for 2 h and 6 h, thermally treated at 600°C and analysed after 1 day (d) and 1 month (m).

inability of Cd to enter into the crystal lattice of zincite in the course of mechanochemical synthesis in proportions greater than 2%. However, it is somewhat confusing to find CdCO_3 phase instead of CdO, having in mind that the samples were subjected to thermal treatment, where CdCO_3 should have been decomposed to CdO. It is expected the CdCO_3 phase was formed in the course of mechanochemical process, as a consequence of excess Cd that did not enter the ZnO lattice. The thermal treatment decomposed CdCO_3 to CdO. However, prolonged aging in ambient conditions (up to a week) caused re-carbonization of the CdO and again formation of CdCO_3 [21].

In order to investigate the possibility of avoiding otavite appearance through increased duration of the synthesis, the sample with 5% of Cd has been milled for 6 h, and thereafter thermally treated. XRD patterns of this sample in comparison with sample milled for 2 h are shown in Figure 2. As can be observed, a new phase, **montepionite**, CdO (ICDD PDF No. 5-640), appears in XRD pattern. How-

Figure 3: The dependence of zincite lattice parameters on cadmium share. The line has been introduced as a guideline for the eye.

ever, the appearance of CdO was found to be the consequence of the immediate XRD analysis. Namely, immediate analysis did not allow for carbonisation induced by ambient conditions. The sample was kept in a capped but not sealed glass container. Analysis of the same sample was repeated after one month, and the majority of monteponite (CdO) has been transformed to otavite ($CdCO_3$) (Figure 2), explaining and confirming qualitative presence of otavite in previous samples (Figure 1).

However, the transformation of monteponite to otavite was obviously much faster in sample milled for 2 h. The reason why this transformation in the ZC5 sample milled for 6 h required much more time (still unfinished after 1 month), was found in different susceptibility to air atmosphere. Namely, the diffraction pattern shows coarseness of monteponite crystallites, that may offer argumentation for slow transformation. In the pattern of sample milled for 6 h, monteponite peaks appear narrow which points out to coarser crystallites. Since the reaction of monteponite with carbon dioxide is a diffusion controlled process, more coarse crystals presume greater diffusion paths and thereby slower reaction rate. In addition, the prolongation of milling also brought about certain increase of corundum peaks intensities, pointing out to greater amount of corundum in sample due to greater mill and balls wearing. Increased presence of inert phase also contributes to decreased air contact and thereby to slower reaction rate.

Close inspection of Figure 1 reveals that diffraction peaks in patterns of doped samples are shifted to lower angles due to unit cell expansion in order to accommodate cadmium ions. Therefore, patterns were de-convoluted and obtained angles used for calculation of lattice parameters through UnitCell program [18]. In Figure 3 the zincite lattice parameters a and c have been shown as a function of cadmium share. According to ICDD PDF No. 36-1451 pa-

rameters a and c of pure zincite are 3.249 Å and 5.206 Å, respectively. Slightly lower values of non-doped sample zincite parameters of $a=3.2472$ Å and $c=5.2022$ Å, were calculated. This could be indication of slight lattice contraction which is known to occur in nanocrystals due to surface tension [22, 23]. On the other hand, increase of lattice parameters with cadmium share could be expected for doped samples since radius of Cd^{2+} is greater than radius of Zn^{2+} . While crystal radius of Zn^{2+} in tetrahedral coordination is 74 pm, radius of Cd^{2+} in same coordination yields 92 pm [24, 25]. Indeed, the increase of both lattice parameters can be observed for sample doped with 1% of Cd, with further increase for the sample doped with 2% of Cd. However, further rise of dopant share yield with no increase of lattice parameters and it appears that no more than 2% of Zn in zincite crystal lattice can be replaced with Cd in the course of mechanochemical synthesis. This finding is in agreement with previous observation of appearance of otavite in samples with more than 2% of Cd. Literature offers two reasons for inability to dope nanocrystals using certain synthetic scheme: expulsion of dopant ions to the surface of nanocrystals by the intrinsic process of self-annealing [9] and inability of the ions to adsorb to the exposed surfaces of the nanocrystals [26].

Close inspection of diffraction peaks reveals another fact (Figure 1), namely, the peaks of doped samples are slightly narrower than those of non-doped sample. In doped crystal lattice one would expect peak broadening due to a strain induced by dopant incorporation. However, according to Figure 1, slight narrowing of the peaks could be solely due to increase of the crystallite size. From the broadness of (101) zincite XRD peaks (Figure 1) ZnO average crystallite size was calculated using the Scherrer's equation and presented in Table 1. As can be observed, crystallite size of non-doped sample is 48 nm while doped samples have crystallite sizes between 57 and 91 nm. Although samples persist its nanocrystalline character, i.e. crystallite size below 100 nm, it appears that doping appreciably influences crystallite size. Despite doping with Cd obviously promotes crystal growth, the changes in crystallite size occur regardless of the doping content.

In order to gain some additional information on doping process outcome, FTIR spectra of $Cd_xZn_{1-x}O$ samples were investigated (Figure 4). The peak between 3200 and 3700 cm^{-1} corresponds to vibration of intermolecular hydrogen bond (O-H) existing between the water molecules adsorbed on the surface of the particles [27, 28]. Bands between 2300 and 2400 cm^{-1} (not shown) appear due to atmospheric CO_2 [27]. Band due chemically adsorbed water molecules appears around 1540 cm^{-1} [17]. Bands centred at 670 cm^{-1} are attributed to corundum [29]. Finally, IR ab-

Figure 4: FTIR spectra of mechanochemically prepared samples with various shares of dopant. Inset: portion of the spectra of samples ZC0 and ZC5 between 1650 and 1250 cm^{-1} .

Table 1: The dependence of zincite crystallite size, bandgap and specific surface area on cadmium share.

	d (nm)	E_g (eV)	SSA ($\text{m}^2 \text{g}^{-1}$)
ZC0	45 ± 2	3,27	$28,7 \pm 0,1$
ZC1	91 ± 4	3,27	$11,6 \pm 0,1$
ZC2	85 ± 4	3,26	$13,5 \pm 0,1$
ZC3	81 ± 4	3,26	$20,2 \pm 0,1$
ZC4	57 ± 2	3,24	$14,3 \pm 0,1$
ZC5	70 ± 3	3,24	$18,7 \pm 0,1$

sorption band typical of ZnO, according to literature occurs between 400 and 500 cm^{-1} [27, 28]. However, additional band appears between 1300 and 1550 cm^{-1} in samples doped with 3, 4 and 5% of cadmium. Inset in Figure 4 clearly shows the superposition of the two bands in the mentioned wavenumber span. The band centred at 1400 cm^{-1} , corresponds to vibration frequencies of carbonate groups (C – O and C = O), [28] and its appearance is consistent with the presence of otavite.

UV-Vis diffuse reflectance spectra and Tauc's plots of non-doped and Cd-doped samples are shown in Figure 5. On the basis of Tauc's plots for direct band-gap semiconductor $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ band-gaps were determined. Band-gap of non-doped ZnO yield 3.27 eV which is fairly close to literature data (3.37 eV) [5]. The band-gap values for ZnO could vary between 3.2 and 3.4 depending on the preparation method [10]. Doped samples show faint redshift of reflectance spectra (Figure 5) and consequently small decrease of band-gap (Figure 5, inset, Table 1) thus enabling some increase of electron-hole formation rate and slightly higher photocatalytic efficiency.

Figure 5: UV-Vis DRS spectra and Tauc's plots (inset) of mechanochemically prepared samples with various shares of dopant.

A decrement of a band-gap with Cd doping was reported by many authors, a good analysis of literature reports on this issue was given by Kumar and Srivastava [30]. Zhang and Zeng [4] attribute red shift of the Cd-doped ZnO to the formation of defect energy level in the ZnO band structure. However, taking into consideration that the band gap of CdO of 2.3 eV is much smaller than of ZnO and that a substitutional type of doping was expected to take place one would expect greater narrowing of ZnO band gap. While substitutional doping affects the density of states other types of doping such as interstitial and surface defects affects band gap less [31]. Furthermore, such doping types are more difficult to perceive and quantify. Since in present case doping with Cd doping only superficially affects the zincite semiconducting properties the modality and extent of the Cd entrance in ZnO crystal lattice should be reconsidered.

The substitutional type of doping presumes the exchange of ions with known charge and size and therefore allows accurate prediction of the cell changes and consequently related properties. In the case of interstitial doping, instead of replacement, the other ions enter lattice irregularly, *i.e.* not on designated unit-cell sites, therefore the extent of effects they cause is more flexible and can be predicted far less accurately. For surface defect type of doping, the prediction using bulk structural characterisation is meaningless. For samples prepared using certain type of synthesis, one doping type should be predominant. However, for mechanochemical type of synthesis that may not necessarily be the case. The mechanochemical type of synthesis offers various advantages, however, molecular grade homogeneity during the synthesis is not one of them. Namely, the reaction is diffusion governed, meaning

Figure 6: N_2 adsorption - desorption isotherms and pore size distribution (inset) of mechanochemically prepared samples with various shares of dopant.

the specific surface, grains, morphology and micro conditions play the dominant role in the mechanisms of the reaction. Thereby, it is possible to expect slight inconsistencies in structure as well in properties, for samples differing marginally in the dopant contents. Taking into consideration ionic radii of Cd and Zn, substitutional doping should be favoured before interstitial. Taking into consideration nano character of particles, *i.e.* increased surface to volume ratio, as well as low activation energy for some zincite facets, the appearance of surface defects is considerably more plausible.

Although lattice parameters revealed entrance of certain amount of Cd in ZnO crystal lattice, without thorough structural investigation it is not possible to discuss the extent of substitutional vs. interstitial vs. surface doping mechanism of Cd in ZnO using mechanochemical type of synthesis. However, it seems that in this case the mechanisms other than substitutional doping are not negligible. In addition, the substitutional/interstitial/surface doping ratio seems to be different for samples with different Cd doping. It has been reported that for doped ZnO [32, 33] the electrical resistivity of the samples initially decreases with doping, reaches a minimum value, and increases with further doping. Such behaviour was explained by diminishing of substitutional type doping by occupation of interstitial sites. Specific surface area (SSA) is important for materials aimed to be utilized as photocatalyst. 'SSA' has been determined from N_2 adsorption-desorption isotherms presented in Figure 6. Isotherms resemble those of Type IV, characteristic for mesoporous material according to International Union of Pure and Applied Chemistry classification [32]. The hysteresis loops are of type H3. The H3 loop is narrow with two almost parallel and vertical branches,

which points out to narrow pore size distribution. The pore size distribution is displayed in inset in Figure 6. As can be observed, pore size distribution is predominately monomodal and varies mostly in range from 10 to 100 nm. Majority of the pores of non-doped sample (ZC0) are seized between 10 and 50 nm. ZnO samples doped with Cd show increase in the pore size with majority of the pores seized between 20 and 100 nm. Although it is evident that obtained shift in pore size distribution is result of the zincite being doped with cadmium, there is no clear dependence on pore size distribution and Cd content in prepared samples. In addition, the volume content of pores for Cd doped samples significantly decreased. Calculated 'BET' specific surface areas are presented in Table 1 and can be linked to the presented pore size distribution. As can be observed SSA value is the highest for the sample ZC0 being $28.7 \text{ m}^2 \text{ g}^{-1}$, while 'SSA' values for the doped samples vary between 11.6 and $20.2 \text{ m}^2 \text{ g}^{-1}$.

Typical SEM micrographs for non-doped and Cd doped ZnO (2%, 3% and 5%) powders are shown in Figure 7. Both, non-doped and doped samples are consisted of agglomerated nanometer-scale grains. Primary particles of doped samples appear to be more uniform in size in comparison to the non-doped sample. Also, it could be argued that agglomerates found in the non-doped sample seem more compact while agglomerates found in doped samples appears more porous.

The EDS analysis (Figure 8) confirmed the presence of Zn, O and Cd in the investigated samples. The C signals in the EDS spectra is due powder-adhesive carbon tape while the Au signal is due sputtered gold for conduction. Quantitative analyses of Cd lines point out to normalised atomic share of Cd at 2.4, 2.8 and 3.4% for samples doped with 2, 3 and 5% of Cd, respectively. This is entirely in line with the increase of the nominal Cd concentration. The amount of Cd in samples slightly deviates from nominal but still is within the error margin of the EDS measurement. As shown by the XRD analysis the present cadmium is incorporated in both zincite and otavite, while some Cd could repose in amorphous form.

In order to evaluate the effect of doping with cadmium on catalytic efficiency of ZnO, the prepared samples were used as photocatalysts for 'MB' degradation. The UV irradiation-based 'MB' discoloration rate for samples with different doping is shown in Figure 9.

Only a marginal difference between the photocatalytic activities of ZnO and Cd doped ZnO (in various amounts) could be observed. The doping with cadmium was already proven to increase zincite photocatalytic activity [4, 6]. According to Zhang and Zeng [4] the enhancement of photocatalytic efficiency of Cd doped ZnO is due improved sepa-

Figure 7: SEM micrographs of samples ZC0 (a, b, c), ZC2 (d, e, f), ZC3 (g, h, i) and ZC5 (j, k, l).

Figure 8: EDS spectra for undoped sample and samples doped with 2, 3 and 5% of cadmium.

Figure 9: Photocatalytic discoloration of MB over prepared catalysts at room temperature. The lines are introduced as a guideline for the eye.

ration of photogenerated charge carriers. However, in concordance with the determined lattice parameters as well as bandgap, in present case the mechanism of cadmium substituting Zn in ZnO crystal lattice is not sufficient to affect ZnO photocatalytic efficiency. As shown before, regardless of the amount of cadmium added in the synthesis no more than 2% of substitutional Cd entered the zincite structure. Beside substitutional part of Cd doping, Cd most likely forms interstitial and surface defects as well. Therefore, the combination of low amount of substitutional dopant in zincite structure and indistinctive doping type disable significant influence of Cd on photocatalytic performance of ZnO.

Considering presented results, the preparation method and precursors should be selected to allow predominately allow efficient substitutional doping, in addition to stoichiometric demands.

4 Conclusion

The limit of Zn replacement with Cd in ZnO crystal lattice via mechanochemical synthesis with precursors used is only 2%. Presence of larger share of Cd results in phase separation and appearance of cadmium oxide or carbonate. The cadmium content in the solid solution was not affected by prolonged milling interval. The replacement limit has been confirmed by lattice parameters calculations. In comparison with non-doped sample, the ZnO unit-cell parameters increase for samples doped with 1 and 2% of Cd while for greater share of Cd unit-cell parameters increase no further. It has been observed that doping impairs nanocrystallinity without specific trend noted. The changes of band-gap with doping were within the limits of the measurement error. Also, no greater differences in morphology have been observed while EDS analysis confirmed the presence of Cd. Photocatalytic measurements revealed only marginal photo-activity changes for the Cd doped ZnO. The method used was not appropriate for preparing ZnO doped with Cd in substantial amounts.

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