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## ORIGINAL ARTICLE

# Peroxide-based route for the synthesis of zinc titanate powder

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**Abstract** In this work the thermodynamical solubility diagrams of zinc and titanium hydroxides were reviewed in order to determine the conditions for maximum degree of phase composition homogenization of precipitates. Experimental investigation of dependency of titanium peroxohydroxide solubility on solution acidity has been carried out and coprecipitation of zinc ions has been studied. It was concluded that precipitation by constant addition of mixed salts and base solutions into the mother liquor with constant acidity of pH $\sim 8.5$ allows maximizing homogenization of precipitate composition. Thermal treatment process of mixed zinc and titanium hydroxides coprecipitated with hydrogen peroxide was studied using thermogravimetric analysis, differential thermal analysis and X-ray diffraction methods. It was found that precipitates of co-precipitated mixtures of zinc and titanium hydroxides contained impurities of salts precursors of the $Zn(NO_3)_2$ and $TiOCl_2$ at a level of 1%. The experimental data demonstrate the influence of hydrogen peroxide on crystal growth rate of the zinc titanate during thermal treatment. The temperature ranges and kinetic parameters of hydroxide mixture dehydration, decomposition of the titanium peroxohydroxide and precursor impurities were determined.

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## 1. Introduction

Fundamental studies concerning the phase and the characterization of the ZnO–TiO$_2$ system have been done, and five compounds often exist in the ZnO–TiO$_2$ binary system including ZnTiO$_3$ (cubic, hexagonal), Zn$_2$TiO$_4$ (cubic, tetragonal) and Zn$_2$Ti$_3$O$_8$ (cubic) (Dulin and Rase, 1960; Bartram and Slepetys, 1961; Yamaguchi et al., 1987).

Currently, zinc titanates have found practical applications as dye pigments (McCord and Saunder, 1945), materials for radioelectronics (Kagata et al., 1993; Kim et al., 1998a, 1998b; Kim et al., 1999), gas sensors (Yadava et al., 2013; Obayashi et al., 1976), catalysts (Chen et al., 1996; Kong et al., 2009; Wang et al., 2012) and sorbents for desulfurization (Swisher et al., 1995; Lew et al., 1989; Susan et al., 1992). Research on their synthesis is still relevant because of its importance in practical applications (Steinike and Wallis, 1997; Hosono et al., 2004a, 2004b; Liua et al., 2009).

There are a lot of processing techniques for preparing the zinc titanates powders by the solid state reaction method (Dulin and Rase, 1960; Bartram and Slepetys, 1961; Yamaguchi et al., 1987; McCord and Saunder, 1945; Chang et al., 2004; Nikolic et al., 2008) and the sol-gel method (Golovchanski et al., 1998; Mohammadia and Fray, 2010; Sedpho et al., 2008; Hosono et al., 2004a, 2004b; Chang et al., 2002; Zhao et al., 2005; Hou et al., 2005; Mohammad and Maryam, 2011; Nicholas et al., 2011). The conventional solid state reaction method is the most widely used route. However, the ceramics which are synthesized by a solid state reaction require a high temperature and the resulting powders exhibit many undesirable characteristics: large particle size and wide particle size distribution. For upgrading a product of solid state reaction it was proposed to use a mechanochemical activation (Fuentes and Takacs, 2013; Botta et al., 2004) and combustion technique (Ghanbarnezhad et al., 2013). These synthesis methods are based on calcination of solid phase mixed zinc and titanium hydroxides, oxides, carbonates or oxalates, as a final step. The process starts with the formation of a new compound at the particle boundary of reacting compounds, thus successful synthesis requires significant mass transfer. Use of highly dispersed reagents with maximum chemical activity allows decreasing temperature of synthesis and time required for complete transformation. But even in this case the absence of composition microfluctuations is not guaranteed. Because of this use of special grinding techniques is required after calcination, it is obvious that synthesis procedures with the highest degree of reacting mixture homogenization, before calcination, should be considered optimal. In this case the expenses on grinding and high temperature treatment can be minimized, which allows to decrease cost of the final product.

It has been proven that wet chemical synthesis methods allow reducing the influence of initial state of components dispersion and providing highest degree of homogenization of complex oxide materials. Active research on zinc titanate synthesis using solgel method with use of organic compounds of zinc and titanium is being carried out for this reason (Mohammad and Maryam, 2011; Nicholas et al., 2011). However, use of such synthesis methods on industrial scale still has low economical feasibility because of relatively high cost of metal organic compounds.

In our opinion the capabilities of synthesis method of high quality zinc titanate by thermal treatment of coprecipitated hydroxides of zinc and titanate are not realized yet. A common mistake is to neglect the initial composition of used precursor solutions. Einage and Komatsu (1981) showed that in 0.02 M solution of titanium(IV) oxychloride at pH < 1 the peroxocomplexes with composition $[(TiO)_8(OH)_{12}]^{4+}$ can already be observed as predominant species, while polynuclear complexes are almost nonexistent. The possibility of zinc hydroxo complexes polymerization has been studied by Matijević et al. (1962). It was found that at pH ∼ 8 polynuclear complexes are formed with composition $[Zn_{2+n}(OH)_{2n+1}]^{3+}$, while at pH < 6.7 only hydrated $Zn^{2+}$ cations can be found.

According to these data, when solutions of the zinc and titanium are mixed, the titanium solution will be in polynuclear form. Therefore, when the polynuclear titanium complexes are able to form microphases during the precipitation of mixed hydroxides, and therefore, as a result their topochemical reaction with zinc oxide requires prolonged high temperature treatment.

Depolymerization of titanium hydroxo complexes can be achieved by increasing acidity of solution or dilution. Alternatively, it can be achieved by addition of complexing agents that will compete with OH-ions for coordination bounds. Hydrogen peroxide can be used as a complexing agent. It is known, that hydrogen peroxide reacts with Ti(IV) ions resulting in formation of anionic complexes with peroxide-radical ligands $O_2^{2-}$. It can be assumed that introduction of peroxide ligands into polynuclear titanium complexes will cause their destruction, which will provide higher mixing degree of titanium and zinc ions.

It should be noted, that feasibility of using hydrogen peroxide in synthesis of titanates has been proven multiple times (Kumar, 1999; Gijp et al., 1998; Fox et al., 1990; Camargo and Kakihana, 2001; Camargo et al., 2009; Gao et al., 2003). The possibility of decreasing crystallization temperature of zinc titanate has been proven by experimental data (Hosono et al., 2004a, 2004b; Chang et al., 2002), however, usually, the nature of such effect is not discussed. In our opinion the decrease of temperature and/or time required for formation of new phase can be attributed to increased homogenization degree of precursors mixture. There is interest to find experimental data proving this hypothesis.

Solving this problem is difficult, because homogenization degree of solid phase is defined by combination of aggregation and disaggregation factor on each stage of synthesis. For instance, even if mixing of salts is achieved on atomic and molecular levels during their dissolution, the achieved homogenization degree will decrease during precipitation process because of difference of crystallization rates, adsorption-desorption of ions, manifestation of ion occlusion effects or mechanical removal of mother liquor. In addition aggregation-disaggregation processes are characterized not only by compound's nature, but also by precipitation conditions, for instance: concentration and ionic composition of solutions, rate and order of their mixing, temperature, etc. Because of that the definition of optimal conditions for coprecipitation of hydroxides is a non-trivial problem and requires through study.

The aim of our research was to determine conditions of chemical precipitation at which maximum homogenization degree of mixed zinc and titanium hydroxides phase composition is achieved. The influence of hydrogen peroxide on zinc titanate crystallization rate during thermal treatment has been studied. By using TGA, DTA and XRD, the contamination of precipitated hydroxides by precursors has been investigated. The temperature ranges and the kinetic parameters of hydroxide mixture dehydration, decomposition of titanium peroxohydroxide and precursor impurities were determined.

## 2. Experimental

### 2.1. Zinc titanate preparation

0.1 M solutions of equimolar mixtures of $TiOCl_2$, $Zn(NO_3)_2$ and $H_2O_2$ and 0.1 M KOH solution was used. The precipitation was carried out by gradual addition of small portion of potassium hydroxide and mixture of zinc and titanium salts with hydrogen peroxide into 500 ml of distilled water. The pH of reacting solution was constantly kept in 8.5 ± 0.25 range. The suspension was continuously stirred by the propeller mixer at 300 rpm. The precipitates were decanted and washed multiple times with $3 \cdot 10^{-6}$ M KOH solution (pH ∼ 8,5) to remove chloride, nitrate and excess potassium ions, until washed off water didn't react with silver nitrate, diphenylamine and sodium hexanitritocobaltate(III). Afterward, all precipitates were vacuum filtered using Büchner funnel, washed with isopropyl alcohol and vacuum dried at 50 °C. All used reagents are pure and analytical grade ("Reachim" Ltd., Sigma Aldrich).

### 2.2. Zinc ions coprecipitation

The experiments of zinc ions coprecipitation were carried out as follows: potassium hydroxide was gradually added to the

mixture of 0.01 M solutions of hydrogen peroxide, zinc and titanium salts to form precipitate of titanium peroxohydroxide. The final pH of reacting solution was in range of 5–6.5. Afterward, the solution was centrifuged to remove the precipitate, and zinc content in solution was determined.
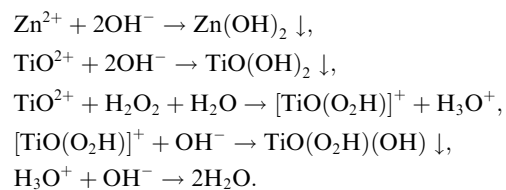
### 2.3. Zinc titanate characterization

Zn–Ti solid materials were characterized by X-ray diffraction (XRD), thermogravimetric analyses (TGA) and differential thermal analyses (DTA). The XRD was performed on a PANalytical X'Pert Pro diffractometer (monochromatic Cu $K_{\alpha 1}$ radiation with wavelength $K_{\alpha 1} = 1.54056$ Å and linear correction with wavelength $K_{\alpha 2} = 1.54433$ Å). The precipitates were studied also by thermal diffraction method with programmed cycle of heating and registering of diffraction patterns stages in temperature range of 40–700 °C with 20 °C step, heating rate 12 °C/min and isothermal aging during 55 min to record each diffraction pattern.

The thermal analysis was performed on a differential scanning calorimeter Thermal Analysis Instruments SDT 2960 in the temperature range 20–600 °C in nitrogen flow (50 ml/min) with a heating rate of 10 °C/min. After heating, the sample was cooled at the same rate of 10 °C/min.

## 3. Results and discussion

### 3.1. Theoretical analysis of chemical precipitation of mixed Zn (II) and Ti(IV) hydroxides

The possible transformations in $Zn(II)-Ti(IV)-H_2O_2$ system were viewed as combination of precipitation, complexing[1] and neutralization reactions:

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow,$$
$$TiO^{2+} + 2OH^- \rightarrow TiO(OH)_2 \downarrow,$$
$$TiO^{2+} + H_2O_2 + H_2O \rightarrow [TiO(O_2H)]^+ + H_3O^+,$$
$$[TiO(O_2H)]^+ + OH^- \rightarrow TiO(O_2H)(OH) \downarrow,$$
$$H_3O^+ + OH^- \rightarrow 2H_2O.$$

It is known, that major precipitation mechanisms of salts with low solubility at constant temperature and pressure are defined by concentration of reagents and acidity of solutions. It is convenient to represent the diagrams of such systems using lgS(pH) coordinates, where S – precipitate solubility (concentration of saturated solution) (Nikolenko et al., 2012). Fig. 1 shows the solubility diagrams for zinc and titanium hydroxides that we have calculated using experimental and literature data. Since there was no data on stability constant of titanium complexes in literature it was not possible to calculate solubility curve for titanium oxyhydroxide in presence of hydrogen peroxide. Because of that, we have studied the dependency of titanium oxyhydroxide on acidity of solution, experimentally. The acquired data are shown in Fig. 1.

The conducted calculations showed that observed shift of titanium peroxohydroxide solubility curve cannot be
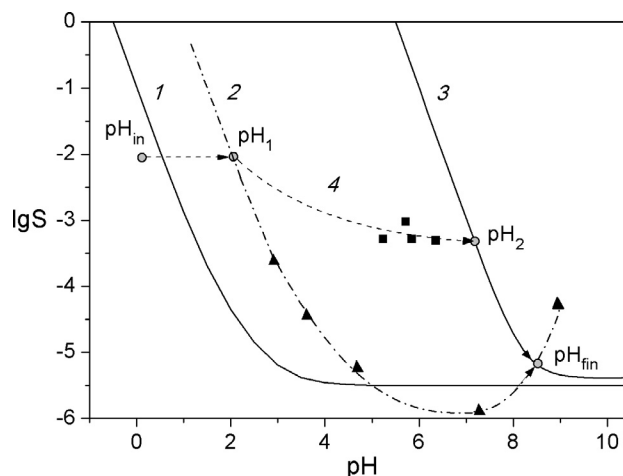


**Figure 1** Solubility diagrams of precipitates: titanium oxyhydroxide (1), titanium peroxohydroxide (2) and zinc hydroxide (2). Curve (4) shows zinc ion content in solution after precipitation of titanium peroxohydroxide from solution with molar ratio Ti:Zn: $H_2O_2 = 1:1:1$.

attributed only to the change of solubility equilibrium. The complexing processes are the main reason for such drastic changes in solubility. From this point of view, it is possible to explain the observed occurrence of titanium peroxohydroxide solubility in basic medium at pH > 8 (Fig. 1, curve 2). Evidently, such solubility is attributed to increased stability of titanium peroxocomplexes because of $HO_2^-$ ligands ionization in Ti(IV) coordination sphere, with formation, for instance, of complexes with composition $[TiO(O_2)(OH)_2]_2^{2-}$ or $[Ti(O_2)_2(OH)_2]_2^{2-}$ (Fox et al., 1990).

We have not established the influence of hydrogen peroxide on the solubility of zinc hydroxide. In addition, the experiments of zinc ions coprecipitation showed that concentration of zinc ions in solution after precipitation of titanium peroxohydroxide decreases significantly. It was determined that at chosen experimental conditions (0.01 M solutions of hydrogen peroxide, zinc and titanium salts) the concentration of zinc ions after precipitation of titanium peroxohydroxide decreases almost by a degree. Since at pH < 6.5 of 0.01 M solution the $Zn(OH)_2$ precipitate does not form, the acquired data should be explained as occurrence of coprecipitation process. Obviously, the reason of such occurrence is attributed to kinetic properties of the system, when the system, because of the diffusion resistance, the condition of thermodynamic equilibrium is virtually unachievable.

Thus, taking into account the occurrence of coprecipitation process of zinc and titanium ions mixture, the precipitation process should be viewed as a chain of three stages:

(1) starting at $pH_1$ a solid phase of titanium peroxohydroxide is form. With further increase of pH the equilibrium concentration of titanium ions changes according to the curve 2 in Fig. 1;
(2) zinc ions are simultaneously coprecipitated with titanium ions (curve 4);
(3) the solid phase of zinc hydroxide starts to form $pH_2$ (curve 3).

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[1] The composition of titanium peroxo complexes depends on pH of solution. Because of that the given equation of titanium peroxo complex formation serves as example of possible complexing reactions (Fox et al., 1990).

Thus, when $pH_{fin}$ is reached the precipitate should include two separate phase: a mixture of titanium peroxohydroxide with coprecipitated zinc ions and $Zn(OH)_2$ phase. In order to determine the precipitation conditions of mixed hydroxides at which highest degree of their mixing is achieved, let's review known methods of hydroxide precipitation:

### 3.1.1. Precipitation method at high supersaturation, in which base solution is added to the mixture of metal salts ($OH^- \rightarrow Me^{n+}$)

With addition of base the pH of solution increases and solid phase of hydroxide is rapidly formed. The order of their formation is defined by their solubility and concentration. As discussed above, the significant difference in solubility of titanium and zinc hydroxide will lead to the formation of precipitate composed of mixture $TiO(OH)_2$ particles, containing coprecipitated zinc ions, and $Zn(OH)_2$ phase.

### 3.1.2. Precipitation method at low supersaturation, in which mixture of salts is added to the base solution ($Me^{n+} \rightarrow OH^-$)

On the contact boundary of $ZnCl_2$, $TiOCl_2$ and KOH a solid phase of hydroxide is rapidly formed. Obviously, that size of primal precipitate aggregates and equalization of concentration in the volume of vessels are defined by mixing rate and particle bond strength of hydroxides in their aggregates. The pH change on the drop surface of mixed salts solution from $pH_{in}$ to $pH_{fin}$ leads to the formation of mixed hydroxides precipitate similar to the described above. As described above, the solid phase can consist of two non-homogeneously mixed phases. However, unlike the previous method, the transition time from $pH_{in}$ to $pH_{fin}$ is reduced significantly, which increases the possibility of zinc ion intake by growing phase of titanium oxyhydroxide. Because of that, the content of $Zn(OH)_2$ phase in formed precipitate is reduced significantly. The limitation of this method is the formation of soluble anionic hydroxocomplexes at pH > 11.5. This makes the usage of the concentrated base solution for precipitation is unacceptable. At the same time, the use of less concentrated base solution isn't feasible either, because the initial quantity of base is defined by quantity of metal salts used, and in the end by quantity of target product.

### 3.1.3. Precipitation method at constant pH, in which solutions of mixed salts and base are gradually added by small portions into the excessive amount of reacting solution ($Me^{n+}$, $OH^- \rightarrow H_2O$)

In the literature this method is called preparation by continuous crystallization at constant supersaturation (Tsevis et al., 1998; Nikolenko et al., 2014). It is known, that the degree of supersaturating is equal to the ratio between product of ions activity of the precipitate in supersaturated solution and such product in saturated solution, and defines the rate of the process. It was proven that even slight changes in degree of supersaturation drastically changes such parameters of crystallizing precipitates as their particle size, polydispersion degree, and even crystal structure. Because of that, keeping the degree of supersaturation at constant level allows increasing reproducibility of chemical precipitation products.

Unlike the first, this method allows conducting the precipitation at relatively fast change of pH in reacting region. However, in the first method the whole solution volume is a reacting region, while in this method it is a separate drop of metal salts solution. This condition is important, because rapid formation of hydroxide shell on the contact boundary of base and metal slats solutions creates new diffusion resistance. This negative influence to homogeneity of forming solid phase because with the increase reaction time the alternating precipitation and re-precipitation of hydroxides can occur based on their solubility.

Also, the advantage of such methods is that it allows carrying out precipitation of titanium and zinc hydroxides at any given pH of reacting solution. For instance, this allows reducing zinc loss, because of the $Zn(OH)_2$ solubility in base solution at pH > 11.5. According to Fig. 1, the optimal pH value for precipitation of equimolar zinc and titanium mixture is ~8.5, because at this value the solubilities of zinc and titanium hydroxide precipitates are almost equal. This condition allows to preserve the stoichiometric ratio Zn/Ti = 1:1 during precipitation stage, thus allowing the preparation of $ZnTiO_3$ samples without zinc oxide or titanium oxide impurities.

Thus, it should be concluded that this method is the best, for precipitation of mixed zinc and titanium hydroxide with highest degree of homogenization.

### 3.2. The influence of hydrogen peroxide on synthesis of zinc titanate

To determine the influence of $H_2O_2$ on the synthesis process of zinc titanate the samples of mixed zinc and titanium hydroxides with and without addition of hydrogen peroxide were prepared. In both cases the precipitation was carried out at the same conditions (pH = 8.5 ± 0.25) by simultaneous addition of solutions of base and mixed zinc and titanium salts to reacting solution. The prepared precipitates after calcinations for 2 h at temperatures of 500, 700 and 900 °C and their X-ray diffraction patterns were studied. Fig. 2 shows the comparison of diffraction patterns taken from mixed zinc and titanium hydroxides samples with and without addition of $H_2O_2$, after calcination at same conditions for 2 h at 900 °C. For comparison, Fig. 2 also shows the diffraction pattern taken from mixed zinc and titanium oxides that was calcinated for 6 h, that matches with references data for cubic $ZnTiO_3$ (JCPDS 39-0190). The formation of crystal phases occurs almost similarly: at first the structure with interplanar spacing 2.5 Å is form (peak at $2\theta = 35.3°$). However, the intensity of this peak for studied samples differs significantly: the sample synthesized with addition of hydrogen peroxides has higher intensity of the peak.

For quantitative comparison of XRD analysis, the intensities of dominant peaks of studied samples are compared using $\ln I(1/T)$ coordinates and shown in Fig. 3. Because samples were calcinated at the same condition, and the peak intensities characterize the crystallinity degree of studied substance, it was assumed that in this case the intensity value can be directly proportional to constant of crystal growth rate. Because of that, we have used coordinates of Arrhenius equation, to determine the influence of hydrogen peroxide on formation rate of $ZnTiO_3$ structure. According to Fig. 3, linear dependencies can be observed for both samples support what is described above.

Thus, the obtained data show that samples prepared with addition of hydrogen peroxide has a higher rate of zinc titanate
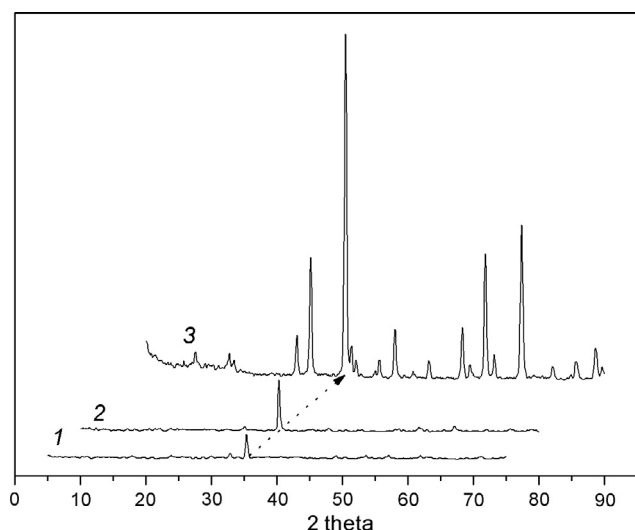
**Figure 2** XRD patterns for mixed titanium and zinc oxides prepared without addition (1) and with addition of $H_2O_2$. (2 and 3), after calcination at 900 °C for 2 h (1 and 2) and for 6 h (3).
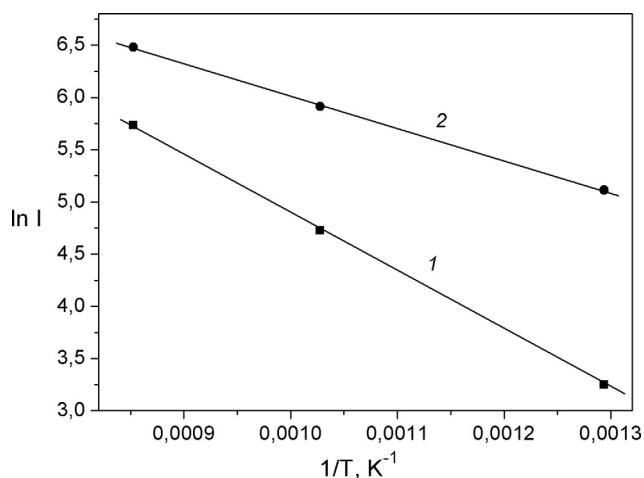


**Figure 3** Comparison of peak intensity logarithm at $2\theta = 35.30°$ of mixed titanium and zinc oxides, prepared without (1) and with addition of $H_2O_2$ (2), vs. reciprocal calcination temperature.

formation than the samples prepared at the same conditions but without addition of hydrogen peroxide. This pattern proves the hypothesis described earlier about necessity of depolymerization of titanium hydroxo complexes prior to coprecipitation with zinc hydroxide.

*3.3. TGA and DTA study of Zn(II) and Ti(IV) hydroxides and activation energy of thermal treatment stage*

The carried out experiments showed that when base solution is mixed with solution of $TiOCl_2$, $Zn(NO_3)_2$ and $H_2O_2$ the yellow X-ray amorphous precipitates are formed. During heating they gradually lose their yellow color and turn white, which can be explain by decomposition of colored peroxocompound of titanium.

To determine the kinetic parameters of thermal treatment process of coprecipitated zinc hydroxide and titanium peroxo-complexes TGA and DTA methods were used. An example of obtained data for the air-dry sample with equimolar ratio Zn/Ti is presented in Fig. 4.

On the DTA cooling curve (dashed line on Fig. 4) no exo- or endothermic effects were observed which allowed using this curve as a base line when interpreting the DTA curve for heating of hydroxide mixture. It was determined, that thermal transformations are accompanied by mass loss until 600 °C. The six segments are observed on TG curve, that are characterized by different rate of mass loss: first segment – 20–120 °C (mass loss 7.8%), second – 120–280 °C (6%), third – 280–350 °C (1.2%), fourth – 350–450 °C (0.8%), fifth – 450–500 °C (mass of the sample didn't change) and sixth – 500–600 °C (0.9%).

The DTA curve shows, that sample mass change occurs with absorption of heat (first endothermic effect with minimum at 86 °C, second – in the 150–280 °C range), but also with its release (four exothermic effects with maximums at 312, 396, 595 °C and wide plateau in the 450–500 °C range).

It is known that heat absorption and mass loss at the initial segments of the DTA and TGA curves of the air-dry oxide and hydroxide sample are attributed to a dehydration process. It should be noted, that in order to prevent particle agglomeration in studied sample resulting from capillary compression force, an isopropyl alcohol was used during drying. Its boiling temperature under air conditions is 82.4 °C. Because of that, the first endothermic effect on the DTA curve should be explained as evaporation of leftover alcohol that was present in pores of sample after vacuum drying at 50 °C.

The change in mass loss rate at 120 °C and sharp turn of the DTA curve at 150 °C, obviously, should be explained by evaporation of adsorbed and hydration water. Considering that this segment of the TG curve stretches up to 280 °C, it should be concluded that in this temperature range, in addition to removal of water from crystals, decomposition of titanium peroxide and full dehydration of zinc and titanium hydroxides also occur. The thermal decomposition of peroxo-groups as part of solid oxide phase was studied by authors (Ivanova et al., 2002). According to their data the peroxo-groups as part of complexes are relatively stable and during heating of oxides are preserved up to 300 °C.

Upon further heating relatively small exothermal peaks at 312, 396 and 595 °C can be observed on the DTA curve. According to the TG curve mass loss at these stages of thermal treatment is 0.8–1.2%, which allowed viewing these effects as a result of decomposition of impurities. It is known, that when relatively concentrated solution is used for chemical precipitation, the formed precipitate usually contains ion traces of accompanying electrolytes. In our case titanium oxychloride, zinc nitrate and potassium hydroxide should be viewed as impurities. From analysis of thermal-chemical properties of these compounds follows that nitrate ions have the lowest decomposition temperature. The decomposition of nitrates occurs with consequential formation of nitrites, oxynitrates and nitrogen oxides. Oxygen and nitrogen are also found among decomposition products. Thus, exothermic effects at 312 and 396 °C can be attributed to decomposition of nitrates to nitrites $(NO_3^- \rightarrow NO_2^- + 0.5O_2 \uparrow)$ with consequential decomposition of nitrites with the release of gaseous products.
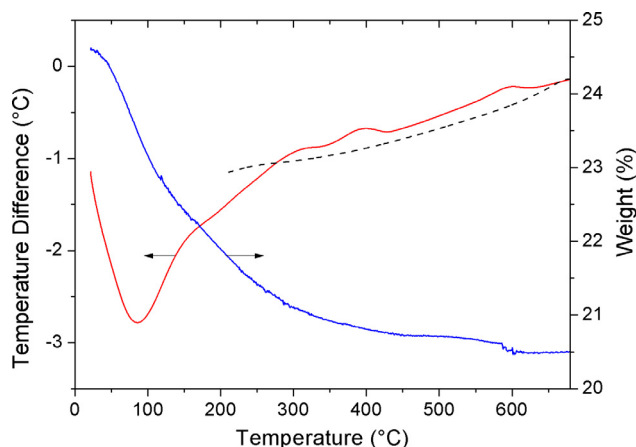
**Figure 4** Analysis results of thermal decomposition of Zn(II) and Ti(IV) hydroxide mixture, coprecipitated from solution with molar ratio Ti:Zn:H$_2$O$_2$ = 1:1:1.

The high temperature of the exothermal effect at 595 °C and mass loss of 0.9% in temperature range 500–600 °C can be explained by decomposition of titanium oxychloride (2TiOCl$_2$ → TiCl$_4$ ↑ +TiO$_2$) with release of gaseous TiCl$_4$.

The data of the TG curve allow determining kinetic parameter of processes that are accompanied by mass loss. For instance, for processes that are described by first-order kinetic equations, the activation energy can be calculated by using, Kissinger's formula:

$$\ln\ln\left(\frac{W_0 - W_k}{W - W_k}\right) = \frac{E_a\Theta}{RT_m^2}, \tag{1}$$

where $W_0$ and $W_k$ – initial and final mass of the sample, $W$ – sample mass at temperature $T$, $T_m$ – temperature at which the maximum rate of mass loss is achieved and $\Theta = T - T_m$.

The order of thermal decomposition reactions can be determined by using data about peak symmetry of the DTA curve (Horowitz and Metzger, 1963). According to the obtained DTA data, the symmetry factors of observed endo- and exothermal effects are close to 1, which indicates that these processes can be describe by first-order equations.

The activation energies for stages of dehydration and decomposition of precursor impurities that are accompanied by mass loss were calculated by using formula (1) and results are presented in Table 1. According to the obtained data, the activation energies decomposition of the zinc and titanium precursors impurities are approximately 5–6 times higher than

**Table 1** Temperature $T_m$ and activation energy for stages of thermal transformations occurring in mixed zinc and titanium hydroxides.

| Stage | $T_m$, °C | $E_a$, kJ/mol |
|---|---|---|
| Removal of isopropyl alcohol | 86 | 40 |
| Dehydration of hydroxides and decomposition of Ti(IV) peroxohydroxide | 200 | 45 |
| Decomposition of nitrate ions | 315 | 255 |
| Decomposition of nitrite ions | 400 | 289 |
| Decomposition of TiOCl$_2$ | 550 | 245 |

that of titanium peroxide decomposition. Such pattern looks logical considering low stability of hydrogen peroxide upon heating.

### 3.4. XRD study and activation energy of grain growth of ZnTiO$_3$ powders

The precipitates were studied by thermal diffraction method with programmed cycle of heating. An example of data acquired for temperature range 100–700 °C with step 100 °C is presented in Fig. 5. It was determined, the formation of highly crystalline cubic zinc titanate (JCPDS No. 39-0190) only occurs at temperature higher than 500 °C.

A more detailed investigation with calculation of interplanar distances showed that transformation of amorphous structure of mixed oxide into crystalline occurs at 580 °C. Fig. 6 shows results of calculating interplanar distance alongside $a$ axis of cubic crystalline structure of zinc titanate during sample calcination. According to this data, the formation of crystalline zinc titanate starts only at 580 °C.

To determine activation energy of ZnTiO$_3$ grain growth stage a dependency of grain size on temperature was used (Chang et al., 2002):

$$\ln D = -\frac{E_a}{RT} + A, \tag{2}$$

where $D$ – average size of grain, $A$ – constant.

Grain size can be determined from XRD pattern. It's known that (Płóciennik et al., 2016) the width of the diffraction peak can be influenced by physical factors characterizing materials such as the crystallite sizes and lattice strains. The source of lattice strains can derive from displacements of the unit cells around their normal positions as well as dislocations, domain boundaries, surfaces, etc. To describe the experimental intensity distribution of the diffraction line derived from these physical factors, different theoretical functions (Gauss- or Cauchy-like function) can be used for the calculations. It is assumed that the diffraction line broadening due to the small size of the crystallites $\beta$ can be expressed by the relation known as the Scherrer's equation:

$$\beta_k = \frac{k\lambda}{D\cos\theta}, \tag{3}$$

where $\beta_k$ (rad) is the diffraction line broadening dependent on the crystallite size, $k$ is the materials constant equal to 0,89, $\lambda$ – wavelength of the X-ray radiation (Å), $D$ – size of the crystallites in a direction perpendicular to $(hkl)$ and $\theta$ – Braggs angle.

Distortion resulting from the lattice strains can be expressed by a dependence known as the Taylor equation:

$$\beta_\text{n} = 4\varepsilon\tan\theta, \tag{4}$$

where $\beta_z$ is the diffraction line broadening dependent on the lattice strains, $\varepsilon$ – describe the lattice strain and $\theta$ – the Braggs angle. Total broadening of the diffraction line is therefore the sum of the $\beta$ and $\beta_z$. Assuming that the particle size and strain contributions to diffraction line broadening are independent to each other and both have a Cauchy-like profile, the observed line broadening[2] is simply the sum of Eqs. (3) and (4):

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[2] For example, the analysis of XRD data showed that half-width of peak at $2\theta = 35.3°$ changes from 0.98° at 600 °C to 0.68° at 700 °C.
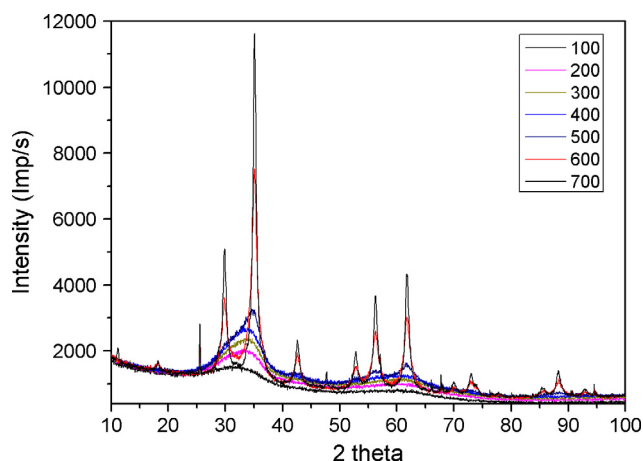
**Figure 5** Analysis result for precipitate with equimolar Zn/Ti ratio using thermal diffraction method. The X-ray pattern for temperature range of 100–700 °C with step 100 °C.
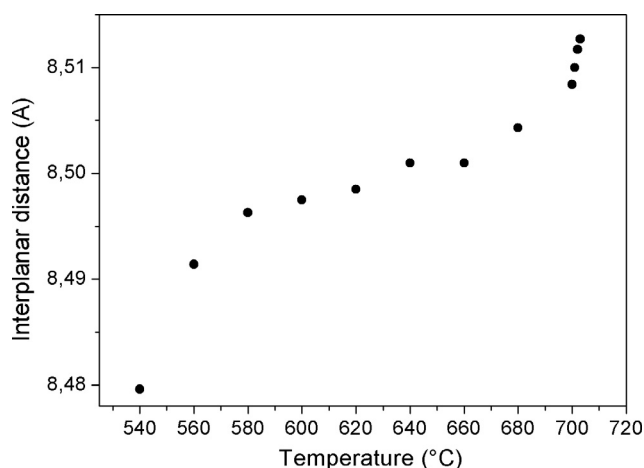


**Figure 6** Evolution of interplanar distance alongside $a$ axis of crystalline $ZnTiO_3$ structure during calcination.

$$\beta = \beta_k + \beta_{\text{я}} = \frac{k\lambda}{D\cos\theta} + 4\varepsilon\tan\theta. \qquad (5)$$

This above equation is known as Williamson−Hall equations. Plotting of the dependence $\beta\cos\theta$ as a function of the $\sin\theta$ for diffraction peaks allows determining the average value of crystallite size (Płóciennik et al., 2016). The calculation using (2) and (5) for 600–700 °C range, showed that the activation energy of grain growth stage is equal to 23.5 kJ/mol. The activation energy for samples that were prepared without addition of hydrogen peroxide is 46.7 kJ/mol.

It should be noted, that according to the data obtained by Chang et al. (2004, 2002), when zinc titanate is prepared by a modified solgel route including the Pechini process, the activation energy for $ZnTiO_3$ grain growth is equal to 20.8 kJ/mol, while during the calcination of zinc and titanium oxides grinded in the ball mill, the activation energy is 48.8 kJ/mol.

In our opinion the decrease of activation energy for $ZnTiO_3$ cubic structure formation stage, prepared by calcination of highly homogeneous mixtures of zinc and titanium oxides, can be explained as follows. It is known, that the condition for thermodynamic equilibrium of solid-state transformation,

as any other chemical process, is an equality of chemical potentials of components in the initial and resulting medium. During interaction of two solid phases the mention equality of chemical potential can be realized through the rearrangement of component in the initial phases with formation of solid solutions, and as a result of formation of new phases with crystalline structure. The component transfer in reacting medium is required in both cases. In thermodynamics it is not required to take the mechanism of such transfer into account, but for chemical kinetics the way of its realization defines the process effectiveness. It is known, that the crystallization process must be viewed as a sequence of at least two stages – formation of crystal nucleuses of new phase and its growing. Obviously, the lower the "local" stoichiometric ratio of zinc and titanium oxide mixture (i.e. stoichiometric ratio in the formation region of nucleus of new crystalline phase), the higher time required for mixing reacting ions, and as a result the lower probability of formation of such nucleuses per time unit.

The connection between mixing degree of components and activation energy can also be explained from point of view of theory of absolute rates of reactions. In the approximate imagination of active complex the reactant particles must not only get close but also to take the configuration of active complex, upon decomposition of which, the final product of reaction is formed. In addition, the free activation energy is defined as a change of enthalpy of activation (defined by chemical nature of the compound), and as a change of entropy of activation. The value of latter component in free activation energy depends not only on the nature of compound (for instance, composition and configuration of intermediate state), but also on entropy value of initial reactants. In our opinion this value is influenced by mixing method of reactants, which defines the "local" stoichiometric ratio of reactant mixture.

### 4. Conclusions

Based on solubility diagram for zinc hydroxide, titanium hydroxide and peroxohydroxide precipitates, the possible mixing methods of metal salt precursors and precipitating agent were analyzed. It was concluded that the most suitable method for the Zn(II)−Ti(IV) system is the continuous crystallization at constant supersaturation. Such precipitation method allows reducing the size of reacting region to a drop of metal salt solution and conducting the precipitation at desired pH value. It was determine that the pH ∼ 8,5 of reacting solution is optimal for coprecipitation of zinc and titanium hydroxides in presence of hydrogen peroxide, because at such acidity of zinc and titanium precipitates have almost equal solubility.

The possibility of partial coprecipitation of zinc ions with titanium peroxohydroxide precipitate, which has been proven experimentally, increases the mixing degree of both metals during chemical precipitation stage. The experiments also prove the hypothesis about role of hydrogen peroxide during synthesis of metal titanates as depolymerizing additive that allows for destruction of polynuclear titanium hydroxo complexes thus increasing the mixing degree of precursor salt solutions. It was determined that addition of hydrogen peroxide during precipitation stage increases crystallization rate of $ZnTiO_3$ phase.

The TG, DTA and XRD methods have been used to study thermal treatment process of mixed zinc and titanium hydroxides precipitated in presence of hydrogen peroxide. The thermal ranges and kinetic parameters of all stages of the process that are accompanied by mass loss have been determined. The thermal analysis method showed that prepared mixed zinc and titanium hydroxide precipitates contain the inclusions of precursor salts – $Zn(NO_3)_2$ and $TiOCl_2$, ∼1% of initial mass of precipitate prior to thermal treatment. It was determined, that decomposi-

tion of such inclusions is characterized by 5–6 times higher activation energy compared to decomposition of titanium peroxohydroxide. The analysis of precipitates by the thermal diffraction method with programmed cycle of heating and diffraction pattern registration showed that the formation of the crystalline cubic zinc titanate occurs in temperature range of 580–690 °C. The change of interplanar distance with further increase of calcination temperature is attributed to polymorph transformation of the cubic zinc titanate into its hexagonal form. The activation energy of $ZnTiO_3$ grain growth was calculated by using the XRD data. For the sample that was prepared with addition of hydrogen peroxide it is equal to 23.5 kJ/mol, while for the sample that was prepared without addition of hydrogen peroxide – 46.7 kJ/mol. A decrease of the activation energy is connected to the degree of stoichiometry of reactant mixtures. In our opinion the degree of stoichiometry compared to the stoichiometry of expected product, should be viewed on macro- and microlevels. On macrolevel the degree of stoichiometry is defined by quantity ratio of the precursor salts in reacting vessel, but "local" stoichiometry is defined by the mixing degree of precursor compounds on atom-molecular level. From this point of view, the selection of precipitation method and conditions should influence on the technical and economic parameters of zinc titanite synthesis process. The results of our investigations on the coprecipitation of zinc and titanium hydroxides in the presence of depolymerizing additive and the literature data on solgel synthesis method of zinc titanate support these conclusions.

The data are in good agreement with the thermodynamics of solid state reactions. As is known, the condition of thermodynamic equilibrium with the solid phase transformation, as with any other chemical transformation is equal of the chemical potential components in the raw materials and reaction products. The equality of chemical potentials in the interaction of the two solid phases can be realized by two methods: or due to redistribution of components in the initial phases with the formation of amorphous phases of solid solutions or by the formation of new phases with different crystal structure (which in fact commonly called the solid phase reaction). Since the chemical potential of a component in different phases of the multiphase system is not dependent on the amount of each phase, the balance can only be achieved by a complete conversion of the initial phases. According to data of the DTA and XRD the crystallization processes of the cubic zinc titanate are not "end-stage" of solid-phase reaction system in the ZnO and $TiO_2$, because the decomposition of the $ZnTiO_3$ is occurring with further temperature increase.

$$ZnTiO_3 \text{ (cubic)} \xrightarrow{800-900\ ^\circ C} 1/2Zn_2TiO_4 \text{ (cubic)} + 1/2TiO_2 \text{ (rutile)}.$$
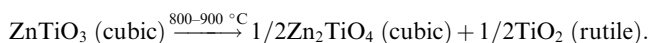
In our opinion, the driving force of the sequential crystal lattice transformation of $ZnTiO_3$ to $\alpha$-$Zn_2TiO_4$ is the formation of a more stable rutile phase. As is known, the rutilization processes of titanium dioxide occur at the temperature of ~850 °C. Obviously, the zinc titanate is relatively stable to the temperature of the anatase to rutile polymorphic transformation and in the system of ZnO–$TiO_2$ has passed the complete conversion of the initial phases.

## Acknowledgments

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