UDK 621.927:661.847.2:549.514

Influence of Mechanical Activation on Synthesis of Zinc Metatitanate

N. Labus[1], N. Obradović[1], T. Srećković[2], V.Mitić[3], M.M. Ristić[4]

[1]Institute of Technical Sciences of SASA, Knez-Mihajlova 35/IV, Belgrade,Serbia
[2] Center for Multidisciplinary Studies, University of Belgrade, Kneza Viseslava 1a, Belgrade, Serbia,
[3]Faculty for Electronic Engineering, University of Nis, Nis, Serbia,
[4]Serbian Academy of Sciences and Arts, Knez-Mihajlova 35/IV, Belgrade,Serbia

Abstract:

Investigations of a ZnO-TiO$_2$ binary oxide mixture during mechanical treatment were mainly focused on obtaining orthotitanate Zn$_2$TiO$_4$ with a spinel structure. Due to the specific way of energy transfer during mechanical treatment using a high-energy ball mill, the system passes through low temperature ZnTiO$_3$ metatitanate phase formation. Mechanical activation was performed on an equimolar ratio mixture of ZnO and TiO$_2$. The anatase phase was previously submitted to heat treatment for achieving a starting mixture rich in a rutile phase. Milling conditions were preset for observing the formation of a low temperature ZnTiO$_3$ phase with a perovskite structure. The powder microstructure was characterized using scanning electron microscopy. A nitrogen gas sorption analyzer with the BET method was used to determine the specific surface area and porosity, indicating changes of powder sample properties during mechanical activation. Also, X ray powder diffractometry was applied to obtain the phase composition. Powders were then pressed into pellets and their compressibility was observed through density changes. According to microstructures obtained by scanning electron microscopy analysis, the system underwent a primary and secondary agglomeration process. Specific surface area measurements supported that conclusion. Compressibility investigations established the difference between compressibility of the non-activated mixture and activated powders. X-ray diffraction analysis revealed that a perovskite structure forms simultaneously with a spinel phase during the process of mechanical activation.

Keywords: ZnO-TiO$_2$, ball milling, zinc titanate, X-ray diffraction, BET method.

Introduction

First investigations of a binary oxide system consisting of ZnO and TiO$_2$ introducing a phase diagram were conducted by Dulin and Race 1960 [1]. The applications for zinc

_____

*) Corresponding author: nebojsa.labus@sanu.ac.yu

titanates were at that time mostly paint pigments and fusion cast thermistors. Zinc-titanate's first application was as a sorbent for removing sulfur from coal gasification products [2-4]. Nowadays, due to the development of microwave dielectrics, zinc-titanates can be used as dielectric resonators and filters in microwave devices [5,6]. Orthotitanate with a spinel structure and cubic lattice is considered the most stabile form of three compounds that coexist in the phase diagram of the $ZnO-TiO_2$ system and as a high temperature titanate form, it was widely investigated [4]. Metatitanate $ZnTiO_3$ with a perovskite structure and with a hexagonal unit lattice is also a good candidate for microwave resonator materials [7], and also as a catalyst [8]. A third most commonly mentioned form of titanate is $Zn_2Ti_3O_8$. It is declared as a low temperature cubic form of $ZnTiO_3$ [9].

The most common way for obtaining metatitanate $ZnTiO_3$ is the sol-gel method [9,10]. It provides fine and homogeneous $ZnTiO_3$ particles with a high specific surface area. In such a way, because the diffusion path is reduced, the temperature needed for synthesis in the subsequent thermal treatment is lowered. Low temperature is required for the formation of $ZnTiO_3$ because of the decomposition of $ZnTiO_3$ to Zn_2TiO_4 and rutile at 945^oC. Recently zinc-titanate was obtained by a solid state reaction [11], which was avoided since a very narrow temperature interval is reserved for obtaining pure $ZnTiO_3$ as it slowly passes from the $Zn_2Ti_3O_8$ cubic form to pure hexagonal $ZnTiO_3$, and decomposes at about 950^oC to Zn_2TiO_4 and rutile [9]. The solid-state route is simple to operate but needs high temperatures and produces powders with a large particle size. Very recently, high energy ball milling was conducted on the $ZnO-TiO_2$ system in order to obtain the most stable phase of orthotitanate Zn_2TiO_4 [12,13], where intensive milling conditions enabled low tempearture titanate forms. The purpose of this work is to investigate events in the early stage of mechanical activation within the $ZnO-TiO_2$ system.

Experimental procedures

The starting materials were commercially available ZnO (99.9% Kemika-Zagreb) and TiO_2 (99.9% Alfa product-Ventron). Thermal treatment was conducted on TiO_2 powder to induce the phase transition from anatase to rutile. Heat treatment consisted of 3 times 8 hours at 1000^oC. Appropriate amounts of ZnO and TiO_2 were weighed in the ratio of 1:1. The powder mixture was afterwards placed in 500 cm^3 volume zirconium oxide vessels together with zirconium balls 10 mm in diameter and the ball to powder ratio was estimated as 20:1. The powders were submitted to mechanochemical treatment in a planetary ball mill device (Fritsch 'pulverisette' 5) with the angular speed of the supporting disk set on 400 rpm. The overall time of milling was 160 minutes and the changes were observed in the following intervals: 5, 10, 20, 40, 80, 160 minutes. Powders were then sieved through a 0.2 mm sieve.

X-ray diffraction patterns of powder mixtures after milling were obtained using a Norelico-Philips PW 1050 diffractometer with λCuK_α radiation and a step/time scan mode of $0.033^o/1s$. The morphology of obtained powders was characterized using a JSM 5300-JEOL, 30 kV scanning electron microscope. The specific surface area was determined with a Micromeritics InC. ASAP 2000 V1.03 sorbtomate with gas nitrogen analysis at -196^oK using the BET method.

The binder-free powders of non-activated and activated mixtures were compacted using the uniaxial double action pressing process in an 8 mm diameter tool (Hydraulic press RING, P-14, VEB THURINGER). The compaction pressure was varied from 49 MPa to 883 MPa to investigate powder behaviour during compaction. Specimen density was calculated from precise measurements of the specimen's diameter, thickness and mass.

Results and discussion

Specific surface area changes are presented on fig 1.
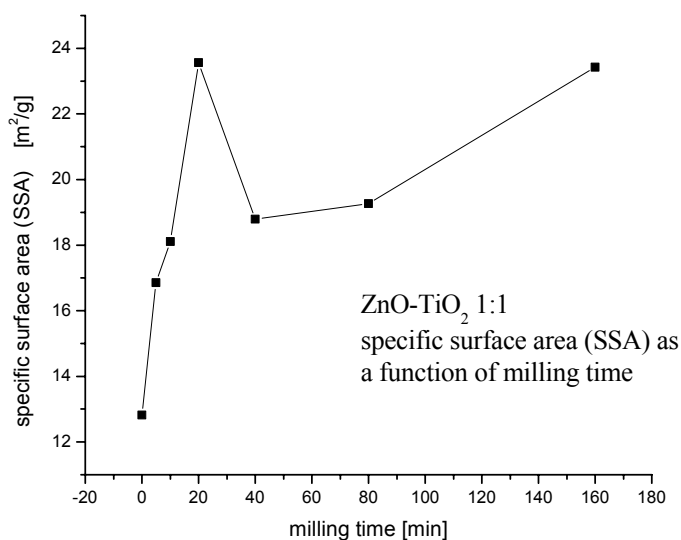
Fig. 1 Specific surface area determined using the BET method as a function of the milling time.

During the first 20 minutes of activation SSA increased from approximately 12 to 24 m^2/g. The second period of mechanical treatment until 40 minutes, regarding the specific surface area, is intensive decreasing from 24 to 19 m^2/g. The milling process consisted of two consecutive processes, namely breaking particles and secondary agglomeration originating from plastic flow. The rise and fall of SSA is subscribed to these processes in that particular order of appearance. A third period from 40 to 180 minutes of mechanical treatment, where SSA slowly increased from 19 to 23 m^2/g, is assigned to the mechanochemical reaction and formation of new phases. Since we are following evolvement of phases that exist in a low temperature region, the chemical reaction passes through the formation of three different phases: Zn_2TiO_4 orthotitanate, $ZnTiO_3$ metatitanate, and TiO_2 rutile. The specific surface area increased at the end of the observed period because the reaction is not finished and gravitates to the most stabile orthotitanate Zn_2TiO_4 form.

SEM characterization on fig. 2. reveals events during mechanical treatment. The non-activated mixture on the scanning electron micrograph (a) has large edge shape particles originating from the rutile phase obtained from anatase in a phase transition during thermal pretreatment. After 5 minutes of mechanical activation (b) we can see that due to the process of fracture, particles are smaller compared with the non-activated mixture and also different in size. The sample activated 10 minutes (c) has particles without any geometrical form together with particles approximately 0.3 micrometers in size that are agglomerated. The powder that was submitted to 20 (d) minutes of activation has particles that are different in size in the range from 0.2 to 0.5 micrometers, respectively, but not agglomerated. Particles activated 80 minutes (e) are most uniform in size, which can be subscribed to the presence of a mechanochemical reaction. Powders activated the maximal time observed (f) are edge shaped large particles in size of 1 micrometer and small particles of 0.2 micrometers indicating evolving of different phases.
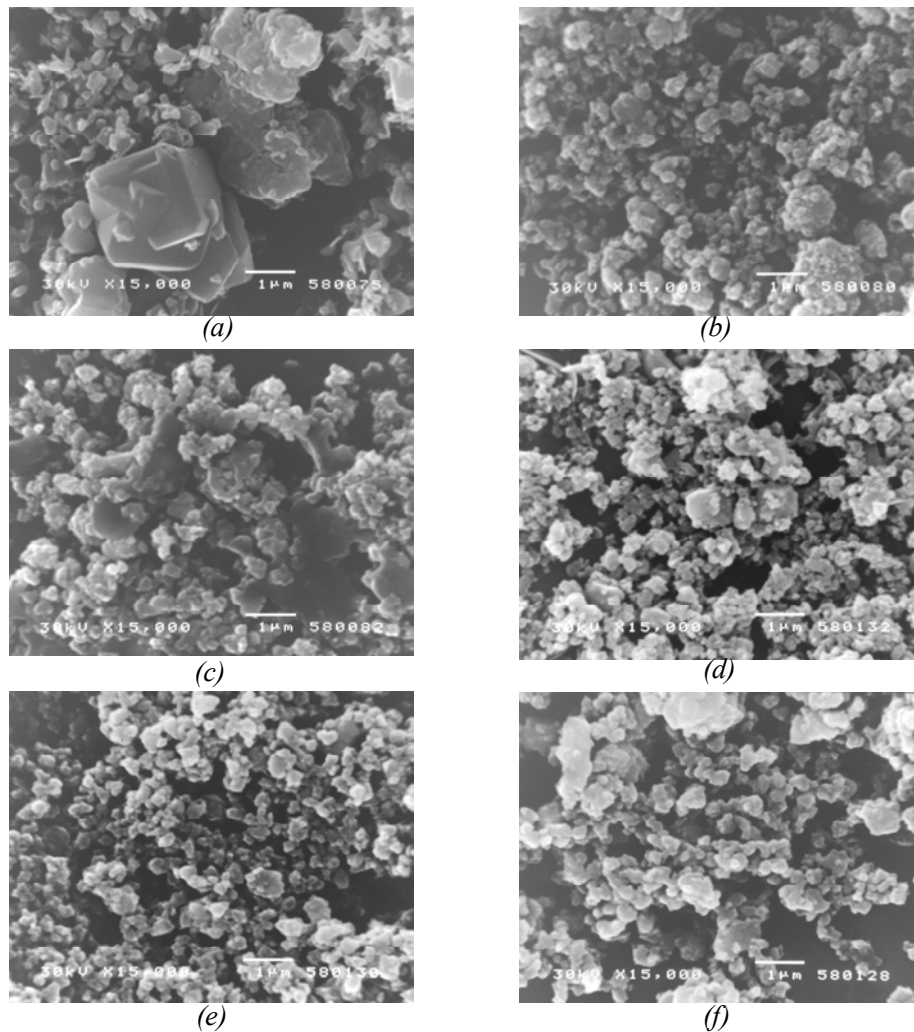
Fig. 2 SEM micrographs for the ZnO-TiO$_2$ system 1:1 mechanically activated for different times a) non-activated mixture, b) 5 minutes, c) 10 minutes, d) 20 minutes, e) 80 minutes and f) 160 minutes.
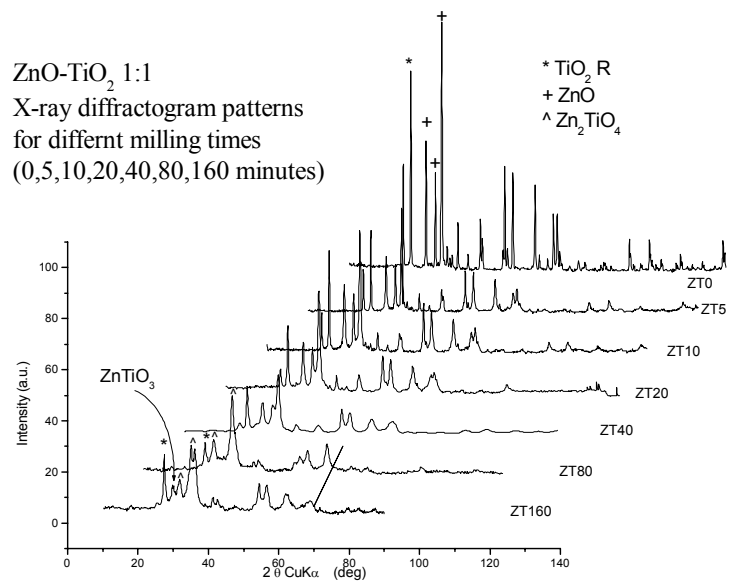
Fig. 3 XRD profiles of ZnO-TiO$_2$ powders 1:1 mechanically activated for different times   (0, 5, 10, 20, 40, 80 and 160 minutes).

X ray diffraction patterns on figure 3 are sorted in the order of descending times of mechanical activation and labeled with times of milling as ZT 0, for the mechanically non activated mixture and ZT 5, ZT 10, ZT 20, ZT 40, ZT 80 and ZT 160. Diffracotogram patterns of powders activated 5, 10, 20 and 40 minutes show sharp reflections of the starting ZnO and TiO_2 oxides. During the activation time intensities of peaks lower significantly. First detectable traces of product phases are visible for times of milling denoted as ZT 80 and ZT 160. Those diffractograms are presented in the enlarged picture on fig. 4.
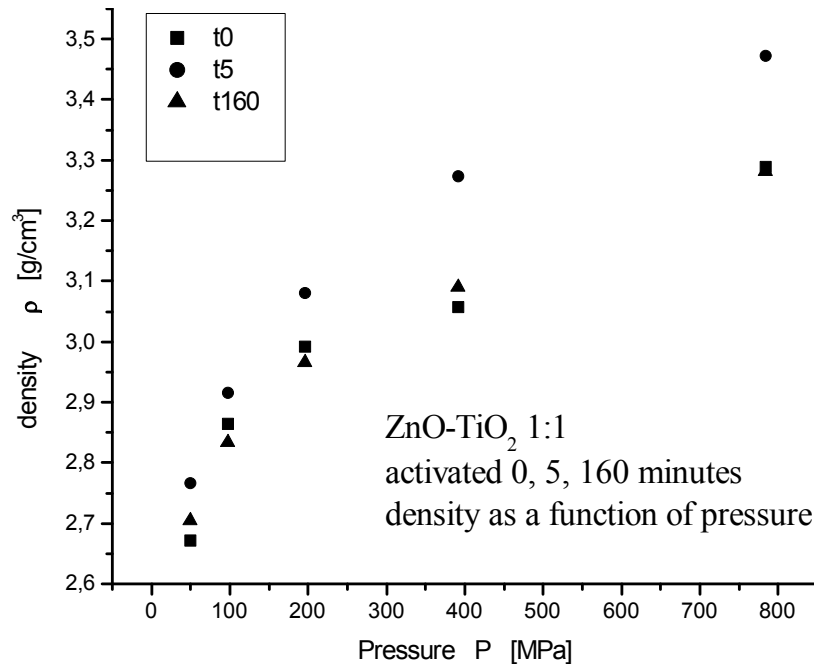
ZnO-TiO_2 1:1
Diffractogram patterns for powders
activted 80 and 160 minutes
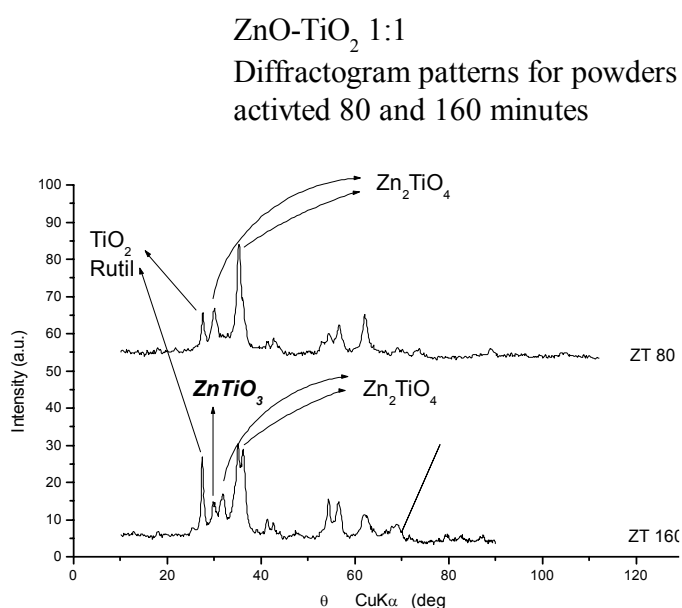
Fig. 4 XRD profiles of ZnO-TiO_2 powders 1:1 mechanically activated 80 and 160 minutes.

80 minutes of activation are zinc orthotitanate Zn_2TiO_4 and a rutile phase. On the diffractogram pattern for the milling time of 160 minutes, together with zinc-orthotitante and rutile reflections, a reflection characteristic for metatitanate $ZnTiO_3$ occurred. The rutile reflection intensity has increased on this pattern. Diffractograms with this number of phases are very difficult to denote due to overlapping of reflections, especially for the step-scan ratio used here. However, the presence of three different phases is clearly visible. It is also important here to emphasize that a third form of titanate, namely $Zn_2Ti_3O_8$ is not considered, since it can be regarded as a low temperature cubic form of hexagonal $ZnTiO_3$, consisting of identical TiO_6 octahedrons, with the same angle position of reflections, but different intensity proportion [9]. The purpose was obtaining zinc-metatitanate. Besides using the stichiometric ratio of 1:1, zinc-metatitanate was aimed for with thermal pretreatment of TiO_2 where the anatase phase transformed to rutile. TiO_2 in a rutile modification is, according to literature [14], more convenient for obtaining a pervoskite structure. Also, the ball to powder ratio was estimated for energy transfer that is more appropriate for obtaining perovskite with mechanical activation in a high-energy planetary ball milling device [15]. Yet, the $ZnTiO_3$ phase was obtained simultaneously with Zn_2TiO_4. All ZnO-TiO_2 phase diagrams presented until now, for the stoichiometric ratio 1:1, predict coexistence of these three phases in a low temperature region bellow 945°C [1,4,6]. A direct parallel between the phase diagram and mechanical activation is not easy to construct. The mechanical treatment route does not enable an physical analysis of the elementary reactive act - impact event. The unique way of energy transfer attached with the milling process does not enable such a comparison.

Only preliminary investigations were conducted of the process of compaction, fig.5. Powders of the non-activated mixture and the mixture activated 160 minutes show a similar

response in density during compaction, while the powder activated 5 minutes achieves the highest densities of all three observed samples. In the non-activated mixture in the range from 200 to approximately 600 MPa, the supposed densification mechanism changes from particle rearrangment to particle deformation mechanism. The value of density then stagnates at around 3.0 g/cm^3. The same course of densification is present for the powder activated 160 minutes, as product phases consisted of particles different in shape and size. The powder activated 5 minutes, is more convenient for compaction since particles have broken and as they are smaller their density constantly increases in the whole observed region.

Fig. 5 Density as a function of pressure in a process of compacting ZnO-TiO$_2$ powders activated for different times: t0-non-activated mixture (0 minutes), t5-activated 5 minutes and t160-activated 160 minutes.

Conclusion

For the milling conditions investigated, it is determined that the reaction simultaneously leads to formation of the phase mixture consisting of zinc-orthotitanate Zn$_2$TiO$_4$ and metatitanate ZnTiO$_3$. After the period of particle breaking until 20 minutes, and the succeeding period of secondary agglomeration, the reaction started after 40 minutes of milling. During compaction the powder activated for 5 minutes showed better compressibility, than the non-activated powder and the powder activated 160 minutes.

Acknowledgement

References

1. F.H. Dulin, D.E. Rase, Phase Equilibria in the System ZnO-TiO$_2$, Journal of American Ceramic Society, 43, (1960) 130
2. S. Ozdemir,T. Bardakci, Hydrogen Sulfide Removal From Coal Gas by Zinc titanate Sorbent, Separation and Purification Technology, 16,(1999) 225-234
3. E. Garcia, S. Cilleruelo, J.V. Ibarra, M. Pineda, J.M. Palacios, Thermogravimetric Study of Regenerable Sulphur Sorbents for H$_2$S Retention at High Temperature, Termochimica Acta, 306 (1997) 23-30
4. J. Yang, J.H. Swisher, The Phase Stability of Zn$_2$Ti$_3$O$_8$, Materials Characterization, 37, (1996) 153-159
5. H.T. Kim, J.D. Byun, Y. Kim, Microstructure and Microwave Dielectric Properties of Modified Zinc Titanates (II), Materials Research Bulletin, Vol.33, 1998, pp. 975-986.
6. H.T. Kim, Y. Kim, M. Valant, D. Suvorov, Titanium Incorporation in Zn$_2$TiO$_4$ Spinel Ceramics, Journal of American Ceramic Society, 84 [5] 1081-86 (2001).
7. H.T. Kim, S. Nahm, J.D. Byun, Journal of American Ceramic Society, 82-12 (1999) 3476.
8. S.F. Bartram, R.A. Slepetys, Journal of American Ceramic Society, 44 (1961) 493.
9. O. Yamaguchi, M. Morimi, H. Kawabata, K. Shimidzu, Formation and Transformation of ZnTiO$_3$, Journal of American Ceramic Society, 70, (1987) C-97-C-98.
10. Y.S. Chang, Y.H. Chang, I.G. Chen, G.J. Chen, Y.L. Chai, Synthesis and Characterization of Zinc-Titanate Nano-crystal Powders by Sol-Gel Techinque, Journal of Crystal Growth, 243 (2002) 319-326.
11. Y.S. Chang, Y.H. Chang, I.G. Chen, G.J. Chen, Y.L. Chai, S. Wu, T.H. Fang, The Structure and Properties of Zinc titanate Doped with Strontium, Journal of Alloys and Compaunds 354 (2003) 303-309.
12. S.K. Manik, P. Bose, S.K. Pradhan, Micrsostructure Characterization and Phase Transformation Kinetics of Ball-milled Preapred Nanocrsytalline Zn$_2$TiO$_4$ by Rietveld method, Materials Chemistry and Physics, 82 (2003) 837-847.
13. T. Sreckovic, N. Labus, N. Obradovic, Lj. Zivkovic, Enhancing Synthesis and Sintering of Zinc titanate Using Mechanical Activation, Materials Science Forum, Vols. 453-454 (2004) p.p. 435-440.
14. U. Steineke, B. Wallis, Formation and Structure of Ti-Zn-Oxides, Crystal Research and Technology, 32 (1997), 187-193.
15. B.D. Stojanovic, Mechanochemical Synthesis of Ceramic Powders with Perovskite Structure, Journal of Materials Processing Technology, 6816 (2003) 1-4.

Резюме: Проведена механическая активация эквимолярной смеси ZnO-TiO$_2$. Отобраны такие услови помола, при которх образуется фаза ZnTiO$_3$ с перовскитной структурой с гексагональной единичной ячейкой. Характеризация морфологии механически активированных порошков проведена при помощи сканирующей электронной микроскопии.Удельная поверхность определена методом БЕТ. Методом дифракции рентгеновских лучей порошков был определен фазовый состав. Исследована компрессибильность механически активированных порошков. При помощи сканирующей электронной микроскопии установлено, что система проходит через первичную и вторичную агломерации, что подтверждается и результатами удельеной поверхности. Проведено сравнивание компрессибильности порошков неактивированных и активированных порошков. Дифракция рентгеновских лучей порошка показала что, перовскитная структура образуется вместе с шпинельной фазой.

Ключевые слова*: ZnO-TiO₂, измельчение шариками, титанат цинка, дифракция рентгеновских лулей, БЕТ метод.*

Садржај: *Механичка активација изведена је на еквимоларној смеши ZnO-TiO₂. Изабрани су услови млевења при којима настаје ZnTiO₃ фаза перовскитске структуре са хексагоналном јединичном ћелијом. Морфологија механички активираних прахова окрактерисана је сканирајућом електронском микроскопијом. Специфична површина одређена је сорбтоматом коришћењем БЕТ методе. Рендгенска дифрактометрија праха дала је податке о фазном саставу. Испитивана је компресибилност механички активираних прахова. Сканирајућа електронска микроскопија показала је да систем пролази кроз примарну и секундарну агломерацију. Специфична површина потврђује овај закључак. Упоређена је компресибилност прахова неактивиране и активараних смеша. Дифрактометрија праха открила је да перовскитска структура настаје заједно са спинелном фазом*

Кључне речи*: ZnO-TiO₂, млевење куглицама, цинк-титанат, рендгенска дифрација, БЕТ метода.*