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Synthesis and Characterization of Zinc Titanate Nano-crystal Powders Obtained by Mechanical Activation

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Abstract:
Development of dielectric materials for microwave frequencies is increasing with rapid progress in mobile and satellite communications systems, where zinc titanates have found application due to their semi-conducting and dielectric properties. Mechanical activation by grinding is a well-known method and common part of the powder preparation route in the field of ceramics. The aim of this work is investigation of the influence of experimental conditions for mechanochemical synthesis of zinc orthotitanate. Starting powder mixtures of ZnO and TiO_2, in the molar ratio that is in accordance with the stoichiometry of zinc titanate spinel type Zn_2TiO_4, were mechanically activated using a high-energy planetary ball mill. The process of mechanical activation was performed during different time intervals from 0 to 300 minutes. Microstructure characterization was determined by X-ray diffraction analysis and scanning electron microscopy. Also, the specific surface area (SSA) of powders samples was measured by a nitrogen gas sorption analyzer using the BET method. The very first traces of zinc titanate are detectable after only 5 minutes of activation. The most interesting occurrence during the mechanical method of activation is that we have an almost pure phase after 90 minutes.
Keywords: *Ball milling, XRPD, SEM, BET, spinel Zn_2TiO_4..*

Introduction

Fundamental studies concerning the phase diagram and characterization of the ZnO-TiO_2 system have been published since 1960s [1]. Three compounds are known to exist in the ZnO-TiO_2 system: Zn_2TiO_4 spinel ortho-titante (cubic), $ZnTiO_3$ perovsikte meta-titanate (hexagonal) and $Zn_2Ti_3O_8$ (cubic). Yamaguchi et al. [2] clarified that $Zn_2Ti_3O_8$ is a low-temperature form of $ZnTiO_3$ only with a cubic unit cell.

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The system still attracts the attention of researchers because of its importance in practical applications. ZnO-TiO_2 system materials were first used in the chemical industry as catalysts and colour pigments [3]. Zinc titanates, particularly Zn_2TiO_4, are nowadays attractive as sorbents, for removing sulfur from coal gasification product gases [4]. In addition, much attention has been paid to their electrical properties leading to numerous applications as solid oxides fuel cells (SOFCs) and as high performance catalysts for the complete oxidation of hydrocarbons or CO and NO reduction [5,6]. Recent progress of microwave devices in the area of mobile telephones and satellite communications brought the need for development of microwave dielectrics with low dielectric loss, high dielectric constant and low-temperature coefficient of resonant frequencies. It has been demonstrated that zinc titanates are good dielectric materials for microwave devices [7-11]. So, they are nowadays widely applied as dielectric resonators and filters [12-17].

It is well known that materials properties depend on synthesis routes, governed by the synthesizing conditions, through their physical and chemical properties. As a low-temperature sintering method is a desirable way for obtaining microwave dielectrics, the sintering temperature as the main parameter, can be significantly lowered without adding any external agent if zinc titanate is prepared in a nanocrystalline form. Mechanical activation is a common part of the powder preparation route in the field of ceramics where high-energy ball milling has become a conventional method for producing nanocrystalline materials.

Many publications pointed out different synthesis routes for obtaining Zn_2TiO_4 (cubic) compound, but unfortunately only few concern Zn_2TiO_4 prepared by mechanical activation, that we are interested in [11,18,19,20].

The aim of the present paper was to investigate the synthesis route and characterization of nanocrystalline form Zn_2TiO_4 obtained from ZnO-TiO_2 at room temperature by high energy ball milling.

Experimental procedures

The starting materials were commercially available ZnO (99.9% Kemika-Zagreb) and TiO_2 (99.9% Alfa product-Ventron). Titan dioxide and zinc oxide had a specific surface area S ~ 12.89 m^2/g and S ~ 13.71 m^2/g, respectively. Appropriate amounts of the compositional constituents in ratio 66 mol% ZnO and 33 mol% TiO_2, that corresponded to the demanded stoichiometric ratio 2:1 were weighed out and the powder mixture was afterwards placed in 500 cm^3 volume zirconium oxide vessels together with balls of 10 mm in diameter (ball to powder mixture mass ratio was 40:1). The mixture labeled as ZTO-000 was not mechanically activated. 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 time of milling was varied from 5 minutes to 300 minutes and mixtures, as appropriate samples, were denoted according to the applied time of activation as ZTO-000, ZTO-005, ZTO-015, ZTO-030, ZTO-090, ZTO-180 and ZTO-300.

X-ray diffraction patterns of the powder mixtures after milling were obtained using a Norelico-Philips PW 1050 diffractometer with λCuK_α radiation and a step/time scan mode of 0.02º/0.4s.

Specific surface area (SSA) of powder samples was measured by a nitrogen gas sorption analyzer using the BET method (Micrometrics In. Co. ASAP 2000 V1.03).

The morphology of obtained powders was characterized using scanning electron microscopy (JSM 5300-JEOL, 30 kV).

Results and Discussion

Results shown in fig. 1 are X-ray diffraction patterns of non-milled and the ball-milled ZnO and TiO_2 powder mixture. ZTO-000 is the X-ray pattern of the starting mixture that contains ZnO and TiO_2. An insignificant amount of a rutile phase is also present in the mixture as a common impurity of the anatase phase. The process of milling in a high-energy planetary mill gave seven succeeding X-ray patterns.

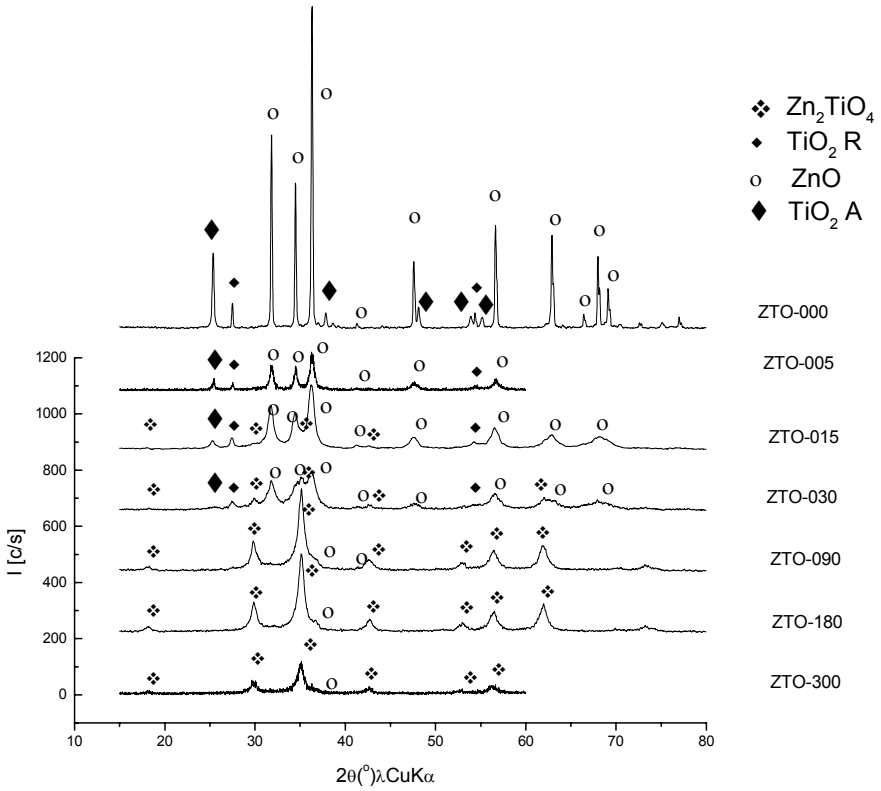


Fig. 1 X-ray diffraction patterns of non-milled and ball-milled ZnO and TiO_2 powder mixture

After 5 minutes of mechanical treatment intensities of all starting phases are significantly lowered, which can be subscribed to the process of particle breaking. Intensive disappearance of an ordered crystal structure is an indicator of extremely high transfer of mechanical energy to the powder during mechanical treatment, due to the type of planetary milling device, and also, high value of powder to balls mass ratio, such as 40:1. After 15 minutes of mechanical treatment the intensity of ZnO diffraction peaks decreased, while peaks of anatase TiO_2 almost completely disappeared. Rutile diffractions, as a high temperature form of TiO_2, shows stability to mechanical treatment, so we can say that, as a reactant, rutile is 'consumed' slower than anatase. In the ZTO-030 diffractogram pattern, all phases are still present, including first traces of a new phase - Zn_2TiO_4. Intensities of ZnO and TiO_2 peaks are lower, while Zn_2TiO_4 peaks are growing.

The diffraction pattern of the powder activated 90 minutes, ZTO-090, shows an almost clear existence of a Zn_2TiO_4 phase. In the course of milling, a α-spinel Zn_2TiO_4 (cubic, space group Fd3m) phase has been formed within 90 min of milling. The ZnO phase has not

been completely utilized to produce the spinel phase and the remaining amount of ZnO cannot be converted further to a spinel-phase just by high-energy ball milling, even though milling is conducted for a much longer milling time.

A well-known problem in the solid-state reaction route, namely ZnO volatilization, can be avoided using mechanical treatment. However, overlapping of most intensive ZnO peaks with most intensive Zn_2TiO_4 peaks is an unavoidable obstacle that is present during the specified mechanochemical reaction with the X-ray powder diffraction method. Diffraction patterns for ZTO-180 and ZTO-300 are very similar to the ones obtained for ZTO-090, since they all mainly contain the Zn_2TiO_4 phase. Diffraction peak intensities of samples activated 90 and 180 minutes are practically identical. Yet, it is obvious that peaks of the sample activated 300 minutes are lower than the previous ones.

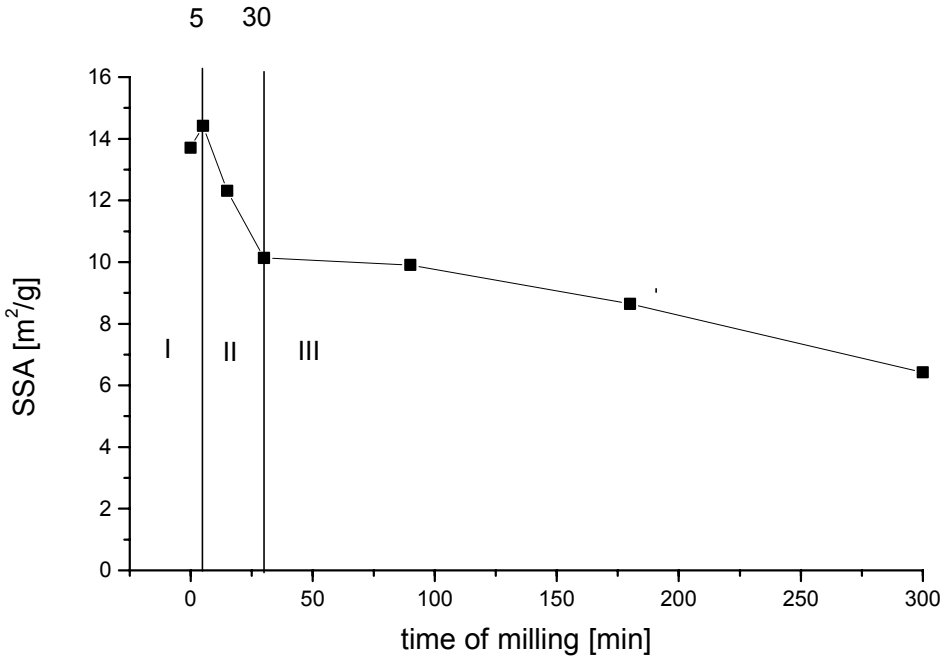


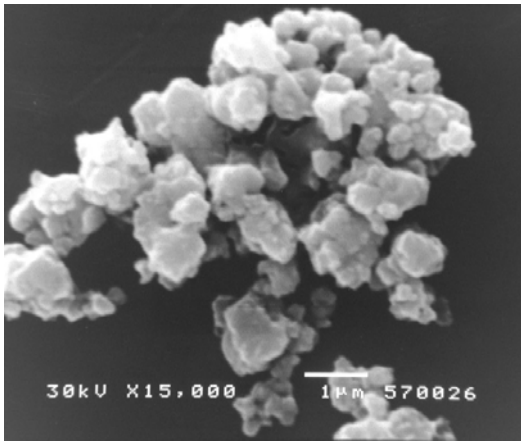
Fig. 2 The dependence of SSA vs. time of milling

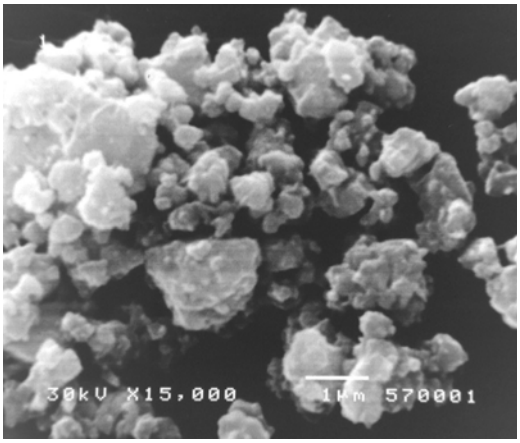
The specific surface area (SSA) of powders samples was measured by a nitrogen gas sorpcion analyzer using the BET method. Fig. 2 shows the dependence of SSA vs. time of milling. It is obvious that the process of milling consisted of three phases: the first phase in the range from 0 to 5 minutes of activation, the second one from 5 to 30 minutes and the third one lasts from 30 to 300 minutes. In the early stage of grinding, the SSA increases from 13.7 to 14.4 m^2/g, then decreases rapidly from 14.4 to 10.1 m^2/g and then slowly (12 times slower than the previous one) decreases till 6.4 m^2/g. Increase in SSA in the first 5 min of mechanical activation leads us to conclude that in the early stage of grinding the process of particle breaking is taking place. After that, from 5 to 30 minutes, rapid decrease in SSA indicates that cold-welding and agglomeration of the starting powders are dominating processes during mechanical activation. Since the first traces of zinc titanate are reported after 30 min of activation, we assume that the mechanochemical reaction of obtaining zinc titanate begins after 30 minutes. With increase of milling time, since there is no further mechanochemical reaction, due to agglomeration, the value of SSA slowly decreases.

Scanning electron images on fig. 3 indicate a slight difference in samples activated

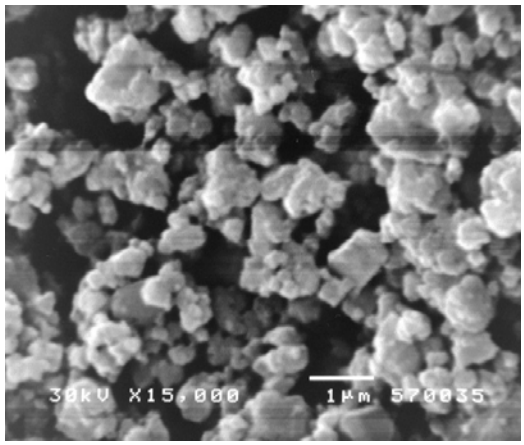
30, 90, and 180 minutes. Irregular shaped sub micron particles, and agglomerates with a size of approximately a few microns are general characteristics for these powders.

ZTO-000





ZTO-180



ZTO-090

Fig. 3 Scanning electron micrographs of various activated powders

Regardless to the previous conclusion made from the analysis based on XRD results in which is pointed out that unreacted ZnO and TiO_2 are still present in ZTO-030 powders besides Zn_2TiO_4 particular phases cannot be distinguished without EDS analysis, since the recognisable polyhedron shape of TiO_2 particles disappears with milling. Powders activated for 30 minutes contain edge shaped particles in size of approximately less than one micrometer. The particle size decreases with an increase in the milling time. Powders activated 90 and 180 minutes definitely consist of particles around 0.5 micrometers in size and agglomerates of zinc titanate. Agglomeration is clearly visible in the powder sample activated for 180 minutes.

Conclusions

Processes concerned with mechanical treatment are hard to comprehend, since the impact process is regarded as a non-equilibrium one, though the results obtained in our investigations lead to better understanding of the complexity of processes and the mechanisms taking place in a planetary mill. The milling time period for obtaining Zn_2TiO_4 is somewhere between 30 and 90 minutes under the conditions used. The period of mixture homogenisation

with intensive particle braking can be rudely estimated to be the period of time from the beginning until 5 minutes of mechanical treatment. The main conclusion based on the analysis is that Zn_2TiO_4 ceramics can be obtained by mechanical activation after a certain time without additional thermal treatment.

Acknowledgement

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Резюме: *С резким прогрессом телекоммуникационных систем разработка диэлектрических материалов, использующихся в микроволновой области, усиливается, причем особое место принадлежит соединениям титаната цинка, благодаря их полупроводниковым и механическим свойствам. Механическая активация измельчением – известный и обычный способ приготовления порошков при получении керамики. Последние достижения в данной области подчеркивают роль химической реакции, протекающей в ходе процесса измельчения. Цель данной работы – изучить влияние экспериментальных условий для механохимического синтеза ортотитаната цинка. Исходные смеси порошков ZnO и TiO_2, молярное соотношение которых*

соответствует стехиометрии шпинельного титаната цинка Zn_2TiO_4, подвергнуты механической активации в высокоэнергетической планетарной мельнице. Механическая активация проводилась в интервале 0-300 минут. Определение микроструктуры проведено методамы дифракции рентгеновских лучей и сканирующей электронной микроскопии. Удельная поверхность порошков определена методом БЕТ. На начальной стадии измельчения до 5 мин. удельная поверхность увеличивается, а потом до 30 мин. резко падает. Последнее указывает на начало процесса агломерации, что установлено и СЕМ микрографиями. Можно сказать, что в данных условиях измерения фаза титаната цинка обнаружена 90 мин. от начала измельчения.
***Ключевые слова**: Механическая активация, дифракция рентгеновских лучей, СЕМ, БЕТ, шпинель.*

***Садржај:** Развој диелектричних материјала који се користе у микроталасној области повећава се са наглим прогресом у телекомуникационим системима, при чему цинк-титанатна једињења налазе своје место захваљујући полупроводничким и диелектричним својствима. Механичка активација остварена млевењем познат је и уобичајен начин припреме прахова у области добијања керамике. Последња достигнућа у овој области наглашавају улогу хемијске реакције која се одиграва током процеса млевења. Задатак овога рада је да проучи утицај експерименталних услова за механохемијску синтезу цинк-ортотитаната. Почетне смеше прахова ZnO и TiO_2, у моларном односу који одговара стехиометрији спинелног цинк-титаната Zn_2TiO_4, су механички активиране коришћењем високоенергетског планетарног млина. Механичка активација посматрана је у различитим временским интервалима од 0 до 300 минута. Микроструктурна карактеризација вршена је методом рендгенске дифракције и скенирајућом електронском микроскопијом. Специфична површина прахова мерена је БЕТ методом. У почетном стадијуму млевења специфична површина се повећава до 5 минута, а онда нагло опада до 30 минута. Смањење специфичне површине указује на процес агломерације који почиње 15 минута након механичке активације, што је потврђено и СЕМ микрографијама. Први трагови цинк-ортотитаната уочени су већ после 5 минута активације. Најважнији закључак је да се током механичке активације скоро чиста цинк-титанатна фаза за посматране услове млевења јавља након 90 минута.*
***Кључне речи**: механичка активација, рендгенска дифракција, СЕМ, БЕТ, спинел Zn_2TiO_4.*