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The Influence of Milling Conditions on Mechanochemical Synthesis and Sintering of Zinc Titanate

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The aim of this work was an investigation of experimental conditions for mechanochemical synthesis and sintering of spinel zinc titanate (Zn_2TiO_4). Starting powder mixtures of zinc oxide and titan dioxide in the molar ratio, in accordance with the stoichiometrics of spinel zinc titanate, were mechanically activated by grinding in a planetary ball mill for various periods of time in the interval of 0 to 300 minutes. Changes of physico-chemical characteristics and microstructure parameters in the $ZnO-TiO_2$ system after grinding were followed using specific surface area analysis and X-ray powder diffraction, while thermal behavior was examined by differential thermal analysis and dilatometry. The beginning of zinc titanate formation was noticed after 30 minutes of milling, and prolonged milling led to the formation of spinel zinc titanate as the major phase with an insignificant amount of unreacted zinc oxide and titan dioxide. The main conclusions based on this analysis are that Zn_2TiO_4 ceramics could be obtained by mechanical activation after a certain time without additional thermal treatment and that sintering temperature as well as the formation temperatures of zinc-titanate are significantly lowered using mechanical treatment.

Досліджено оптимальні умови для механо-хімічного синтезу та спікання титанату цинку шпінелі (Zn_2TiO_4). Порошкова суміш оксиду цинку та діоксиду титану в мольному відношенні, відповідно до стехіометричного титанату цинку шпінелі, механічно активізувалася у планетарному кульовому млині на протязі 300 хвилин. Для різних проміжків часу розмелу

зміни параметрів структури та фізико-хімічних властивостей в системі ZnO−TiO$_2$ спостерігались за результатами аналізу питомої поверхні порошку, картин рентгенівської дифракції, кривих дилатометрії та диференціального термографічного аналізу. Початок утворення цинкового титановокислого формування спостерігається після 30 хвилин механоактиваційного синтезу, а подальший розмел призводить до формування титанату цинку шпінелі з незначною кількістю непрореагованого оксиду цинку та діоксиду титану. Збільшення часу механо-хімічного синтезу сприяє зменшенню кількості домішок та зниженню температури спікання кераміки Zn$_2$TiO$_4$.

Исследованы оптимальные условия для механохимического синтеза и спекания титаната цинка шпинели (Zn$_2$TiO$_4$). Порошковая смесь оксида цинка и диоксида титана в мольном отношении, соответствующему стехиометрическому титанату цинка шпинели, механически активизировалась в планетарной шаровой мельнице на протяжении 300 минут. Для разных промежутков времени помола изменения параметров структуры и физико-химических свойств в системе ZnO−TiO$_2$ фиксировались по результатам анализа удельной поверхности порошка, картин рентгеновской дифракции, кривых дилатометрии и дифференциального термографического анализа. Начало образования цинкового титановокислого формирования наблюдалось после 30 минут механоактивационного синтеза, а дальнейший размол приводил к формированию титаната цинка шпинели с незначительным количеством непрореагированного оксида цинка и диоксида титана. Увеличение времени механохимического синтеза способствует уменьшению количества примесей и снижению температуры спекания керамики Zn$_2$TiO$_4$.

1. INTRODUCTION

Fundamental studies concerning the phase diagram and characterization of the ZnO−TiO$_2$ system have been conducted since the 1960 s [1]. This system still attracts attention due to its importance in practical applications. Although ZnO−TiO$_2$ system materials have been used widely in the chemical industry as catalysts and pigments, as dielectric materials they have only been used as a composition of solid solutions [2]. It has been demonstrated recently that zinc titanates can be used as dielectric materials for microwave devices [3−7]. Due to recent progress of microwave applications in the area of mobile telephones and satellite communications the development of microwave dielectrics having low dielectric loss, high dielectric constant and low-temperature coefficient of resonant frequencies has been intensified so that they can be used as dielectric resonators and filters [8−13].

Also, titanates and related materials are of interest for catalytic

oxidation and reduction reactions associated with the regulation of waste gas emissions from motor vehicles [14−16].

In addition, much attention has been paid to their electrical properties leading to wide applications as solid oxides fuel cells (SOFCs), metal-air barriers, gas sensors, in microelectronics and as high performance catalysts for the complete oxidation of hydrocarbons or CO and NO reduction.

It is well known that the properties of materials depend on their synthesis processes, as their physical-chemical properties are influenced by the synthesis conditions. As low-temperature sintering is a desirable property for microwave dielectrics, the sintering temperature can be lowered down further without adding any external agent, if zinc titanate is prepared in a nanocrystalline form. High-energy ball milling has now become a conventional method for producing nanocrystalline materials [17].

Three compounds are known to exist in the $ZnO-TiO_2$ system: Zn_2TiO_4 (cubic), $ZnTiO_3$ (hexagonal) and $ZnTi_3O_8$ (cubic). Recently, Li et al. [18] reported the formation of a new $ZnTiO_3$ (cubic) phase as precipitates inside the Zn_2TiO_4 matrix with the same structure and lattice parameter of Zn_2TiO_4 phase. Yamaguchi et al. [17] clarified that $Zn_2Ti_3O_8$ is a low-temperature form of $ZnTiO_3$. Zn_2TiO_4 can be easily prepared by a conventional solid-state reaction between $2ZnO$ and $1TiO_2$. Zinc titanates are promising candidates for low-temperature sintering dielectrics, because they can be sintered below 1100°C without sintering aids.

In this paper the influence of milling conditions on mechanochemical synthesis and sintering and properties of zinc titanate were investigated.

2. EXPERIMENTAL

Mixtures of ZnO (99.9% Kemika−Zagreb) and TiO_2 powders (99.9% Alfa product-Ventron) with a molar ratio of $ZnO:TiO_2 = 2:1$ were mechanically activated by grinding in a planetary ball mill (Fritsch Pulverisette 5).

The milling process was performed in air during 5, 15, 30, 90, 180 and 300 minutes at the basic disc rotation speed of 320 rpm and a rotation speed of bowls of 400 rpm. Zirconium oxide balls (approx. 10 mm in diameter) and bowls (500 cm^3) were used with a ball to powder mixture mass ratio of 40:1. Samples were denoted as ZTO-000 to ZTO-300 according to the milling time.

X-ray powder diffraction patterns of the milled powder mixtures and of sintered samples were obtained using a Norelico-Philips PW-1050 diffractometer, with a CuK_α radiation and a step scan mode of 0.02°/0.4 s.

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

Differential thermal analysis was performed using a Shimadzu DTA-50 during non-isothermal heating from 20 to 1050°C with a constant heating rate of 10°C/min, in nitrogen atmosphere and the rate flow of 20 ml/min.

Relative shrinkage of samples obtained by uniaxial pressing of activated powders was followed by a sensitive dilatometer (Bähr Gerдtebau GmbH Typ 702 s) during non-isothermal heating in air up to 1100°C with a constant heating rate of 10°C/min and 1h holding at the same temperature.

3. RESULTS AND DISCUSSION

Starting powders had the specific surface area (SSA) of 11.9 (ZnO) and 12.9 m^2/g (TiO_2). The SSA of non-activated and activated mixtures are given in Table 1.

The increase in surface area leads us to conclude that the process of particle breaking takes place at the beginning of milling (until 5 minutes of activation).

The rapid decrease (5−30 min of activation) in the surface area is an indicator of secondary agglomeration or cold welding [19] of powder mixture and the further decrease (30−300 min) is due to agglomera-
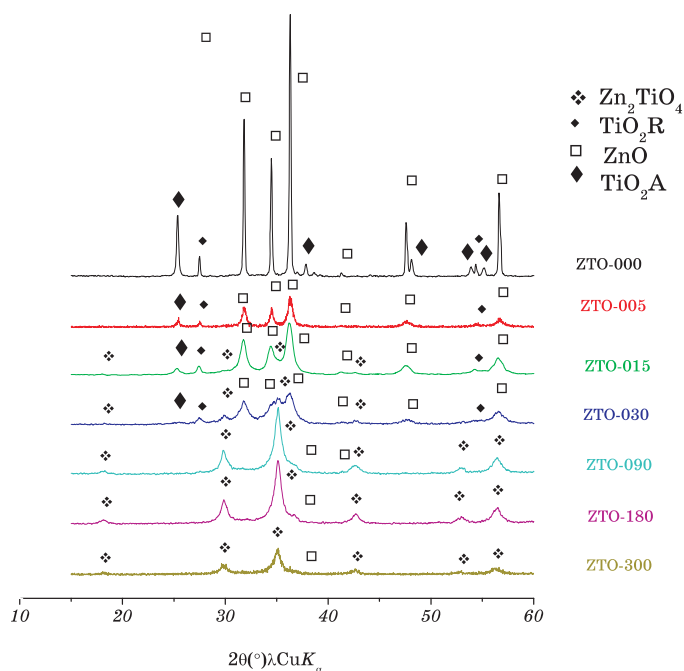

Fig. 1. XRD patterns of non-milled and ball-milled powder mixtures.

tion as the dominant process in this stage of mechanical activation.

X-ray diffraction patterns of non-milled and ball-milled ZnO and TiO_2 powder mixtures are given in Fig. 1. ZTO-000 is the X-ray pattern of the starting mixture containing ZnO and TiO_2. A relatively small amount of a rutile phase is present in the mixture together with the anatase modification of TiO_2 (78% anatase-22% rutile).

After 5 minutes of mechanical treatment intensities of all starting phases are significantly lowered. The decrease of crystallinity that takes place in this type of powder processing is a consequence of defect formation and diminution of crystallite sizes causing peak broadening.

Intensive disappearance of a 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, the high value of powder to balls mass ratio, such as 40:1.

The intensity of ZnO diffraction peaks decreased after 15 minutes of mechanical treatment, while peaks of anatase TiO_2 almost completely disappeared. A larger part of anatase phase is participating in mechanochemical reaction along with ZnO, and the rest of anatase phase disappears probably due to the phase transformation from anatase to the most stabile form of TiO_2-rutile [20, 21].

In the ZTO-030 diffraction pattern, all phases mentioned above are still present, including the first significant peaks of a new phase — Zn_2TiO_4. Intensities of ZnO and TiO_2 peaks are lower, while Zn_2TiO_4 peaks are higher with increasing milling times.

The diffraction pattern of the powder activated 90 minutes, ZTO-090, shows 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 formed after 90 minutes of milling. The ZnO phase was not 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 was conducted for a much longer milling time [1, 20]. The remaining of ZnO implies the remaining of TiO_2 (due to stoichiometry), although peaks of TiO_2 weren't detected. Kim et al. [3, 4] found that Zn_2TiO_4 has a rutile solubility up to 0.33 mole. In this solubility region, a single phase of α-Zn_2TiO_4 was obtained.

A well-known problem in the solid-state reaction route, namely ZnO volatilization, can be avoided using mechanical treatment. Yet, overlapping of the most intensive ZnO peaks with the most intensive Zn_2TiO_4 peaks is an unavoidable obstacle that is present during mechanochemical reaction characterized with the X-ray powder diffraction method.

ZTO-180 is very similar to the one activated 90 minutes, considering that it consisted of a zinc titanate phase.

The process of crystallite attrition takes place in the powder activated 300 minutes.

DTA curves of the non-activated sample and mechanically activated
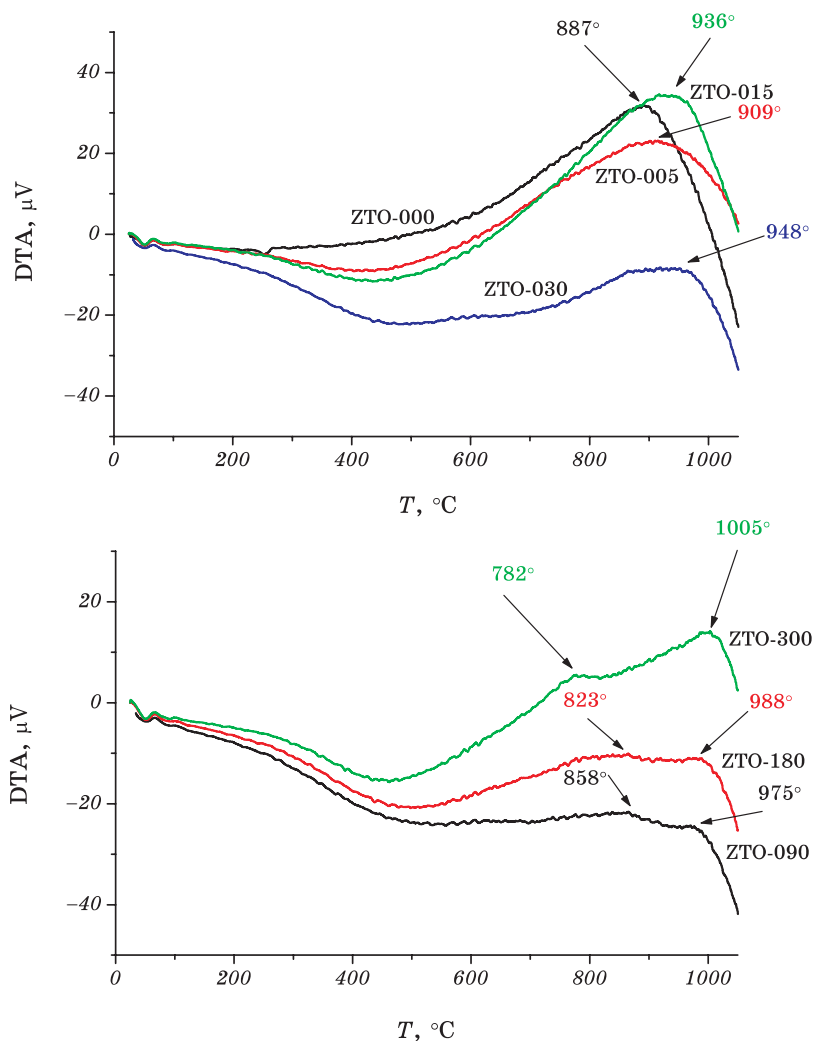
Fig. 2. DTA curves of powder mixtures as a function of milling time.

mixtures are shown in Fig. 2. The results can be divided in two categories. The first one includes the non-activated sample and samples activated for 5, 15 and 30 minutes. One characteristic exo-peak is obvious on the ZTO-000, ZTO-005, ZTO-015 and ZTO-030 curves as a result of the nucleation process and spinel formation [22].

It is seen that DTA curves for ZTO-090, ZTO-180 and ZTO-300 samples have a different shape in respect to preveious group of samples. Exothermal effects are a consequence of two processes.

The first one is due to arrangement of the crystal structure and crossings of ZnO and TiO_2 cations between normal and inverse spinel [20], and
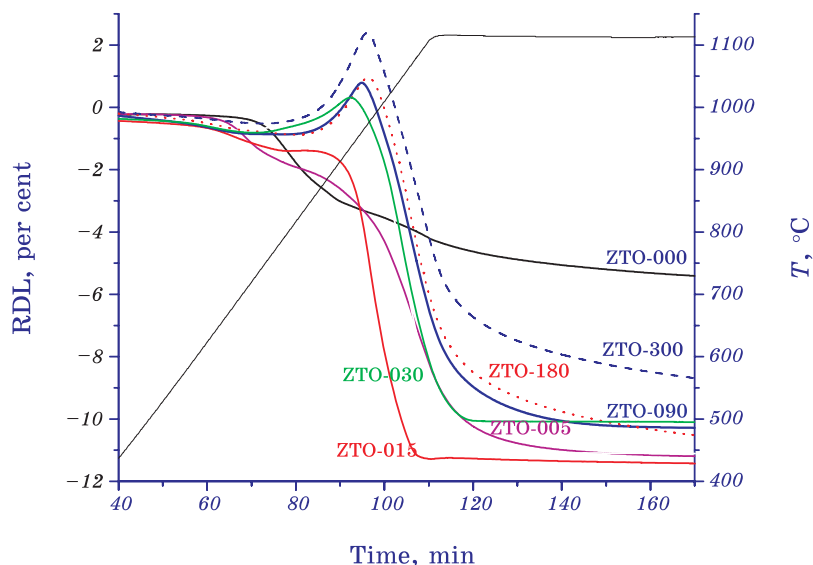
Fig. 3. Relative shrinkage of samples as a function of the heating temperature and the milling time.

the second one is due to crystal growth at higher temperatures [23].

Figure 3 shows the relative shrinkage of samples as a function of time during heating and holding at 1100°C for various activated samples obtained by the dilatometer. Thus, one can notice that for the mixture mechanically activated 15 minutes characteristic shrinkage occurs at 900°C representing intensive sintering. According to the fact that in samples of the mixtures activated for 30, 90, 180 and 300 minutes starting components are still present in lower quantities, regarding the one activated 15 minutes, nucleation induces formation of zinc-titanate as the dominant process. Also, the onset of sintering shifts to higher temperatures for higher times of activation.

Contrary to that, the solid-state reaction in the non-activated mixture, proceeded in quite a different manner. First, in the case of the non-activated sample the characteristic maximum of zinc titanate formation is not observed, and secondly the sintering process of the starting mixture anticipated the solid-state reaction.

Figure 4 shows the X-ray diffraction patterns of ZTO-000, ZTO-015 and ZTO-090 samples sintered at 1100°C for 1 hour.

It is clearly visible that after heating we have a pure Zn_2TiO_4 phase, with a small amount of unreacted ZnO in all samples. It is obvious that the reflections are sharper and more intensive compared to the activated one (see Fig. 1.) due to recrystallization. Recovery of the activated material, the disappearance of defects and grain growth are processes that occur during sintering.
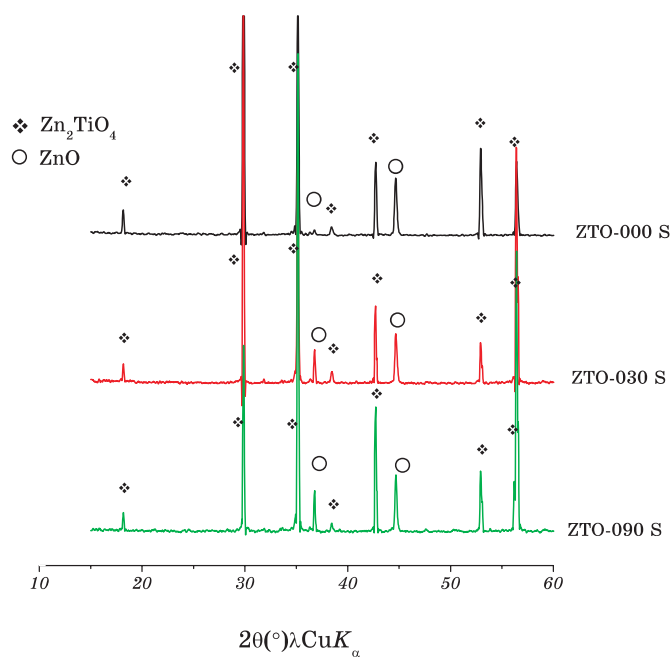
Fig. 4. XRD patterns of ZTO samples sintered at 1100°C for 1 h.

TABLE 1. Specific surface area of non activated and activated samples.

sample	SSA (m^2/g)
ZTO-000	13.7
ZTO-005	14.4
ZTO-015	12.3
ZTO-030	10.1
ZTO-090	9.9
ZTO-180	8.6
ZTO-300	6.4

4. CONCLUSIONS

Formation of spinel zinc titanate (Zn_2TiO_4) and the influence of milling conditions on the mechanochemical reaction in the $2ZnO:1TiO_2$ system were investigated. It was established that the mechanochemical reaction starts after 15 minutes in a planetary ball mill. After 90 minutes of milling, a spinel phase and a small amount of zinc oxide are detected in the powder.

With appropriate thermal treatment, temperatures of sintering and zinc titanate formation are lower than in the case when non-activated mixtures were used.

The main conclusion based on dilatometry and XRD analysis is that 15 minutes activation successfully promotes the solid-state reaction and the sintering process introducing and establishing an optimal ratio between mechanical activation and thermal treatment for sintering and synthesis of Zn_2TiO_4.

ACKNOWLEDGEMENT

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