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Analysis of isothermal sintering of zinc-titanate doped with MgO**N. Obradovic^{1*}, S. Stevanovic¹, M. Mitric², M. V. Nikolic³, M. M. Ristic⁴**¹ Institute of Technical Sciences of SASA, Knez-Mihailova 35/IV, 11000 Belgrade, Serbia,²The Vinca Institute of Nuclear Sciences, Belgrade, Serbia,³Institute for Multidisciplinary Research, Kneza Visaslava 1a, 11000 Belgrade, Serbia,⁴Serbian Academy of Sciences and Arts, Knez-Mihailova 35/IV, 11000 Belgrade, Serbia**Abstract:**

The aim of this work was analysis of isothermal sintering of zinc titanate ceramics doped with MgO obtained by mechanical activation. Mixtures of ZnO, TiO₂ and MgO (0, 1.25 and 2.5%) were mechanically activated 15 minutes in a planetary ball mill. The powders obtained were pressed under different pressures and the results were fitted with a phenomenological compacting equation. Isothermal sintering was performed in air for 120 minutes at four different temperatures. Structural characterization of ZnO-TiO₂-MgO system after milling was performed at room temperature using XRPD measurements. DTA measurements showed different activation energies for pure and doped ZnO-TiO₂ systems. Thus addition of MgO stabilizes the crystal structure of zinc titanate.

Keywords: Pressing, Sintering, XRPD, DTA, ZnO-TiO₂ system.

Introduction

Historically, ZnO-TiO₂ materials have been used as white color pigments and catalysts for the desulphurization of hot coal gases [1,2]. In the last few decades, zinc-titanates have also been used as dielectric materials for microwave devices and, more preferably, for low-temperature co-fired ceramics (LTCC) [3-6].

Phase transitions in the ZnO-TiO₂ system are relatively complex, and sensitive to the start material, additives and the preparation process [7]. Calcination of the ZnO-TiO₂ system can lead to three different phases: ZnTiO₃ (hexagonal), Zn₂Ti₃O₈ (cubic) and Zn₂TiO₄ (cubic) [8-12]. Zn₂TiO₄ is stable from room temperature to its liquid temperature (1418°C), while ZnTiO₃ is stable from room temperature to 945°C, which is the temperature of its separation into Zn₂TiO₄ and rutile-TiO₂. Yamaguchi et al. [10] clarified that Zn₂Ti₃O₈ is a low-temperature form of ZnTiO₃ and is stable at temperatures lower than 820°C. In general, these titanates are prepared by a conventional solid-state reaction, sol-gel method, etc. A number of studies up to now have been devoted to the preparation, compound formation, crystal structure, stability, additives and electrical properties of ZnTiO₃ [13-16], but very few to Zn₂TiO₄ [17,18].

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In this work, Zn_2TiO_4 ceramics with MgO addition were prepared by solid-state reaction combined a chemical processing. MgO has been proved to be an effective sintering aid for zinc titanate ceramics [13,14]. Mechanical activation has been used to shorten the sintering procedure or lower the sintering temperature. In this case the starting powders were mechanically activated for 15 minutes because it has been demonstrated that activation of only 15 minutes very successfully promotes solid-state reaction as well as sintering processes and establishes an optimal thermal treatment of sintering at a significantly lower temperature than in case of non-activated mixture [18]. The phase structure, pressing process as well as thermal behavior of the system were investigated.

Experimental procedure

Zn_2TiO_4 samples with addition of $\text{MgO} = 0 - 2.50$ wt.% were prepared by conventional solid-state reaction method using ZnO (99.99% p.a. Aldrich), TiO_2 (99.99% p.a. Aldrich) and MgO (97% p.a. Merck) powders. The starting materials were mixed in ethanol in a magnetic whisk for two hours and then dried at 120°C for two hours. The powders were submitted to mechanochemical treatment for 15 minutes in a planetary ball mill device (Fritch Pulverisette 5) at the angular speed of the supporting disc set on 400 rpm. Samples were denoted according to the added oxide, ZMTO-0, ZMTO-1.25 and ZMTO-2.50. Powders were then sieved through a 0.2 mm sieve.

X-ray diffraction patterns of powder mixtures after milling were obtained using a Philips PW 1050 diffractometer with λCuK_α radiation and a step/time scan mode of $0.05^\circ/1\text{s}$.

The binder-free powders 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 0.5 to 9 t/cm^2 (49-883 MPa) to investigate the behavior of powders during compaction.

Differential thermal analysis was performed using a Shimadzu DTA-50 during non-isothermal heating from room temperature to 1100°C with a constant heating rate of $10^\circ\text{C}/\text{min}$ in air atmosphere.

Compacts pressed under 4 t/cm^2 pressure were placed in an alumina boat and heated in a chamber furnace (Heraeus). When the temperature of the furnace achieved 800, 900, 1000 and 1100°C , compacts were sintered isothermally in air atmosphere for 5, 15, 30, 60 and 120 minutes.

The density of specimens was calculated from precise measurements of specimen's diameter, thickness and mass.

Results and discussion

X-ray diffraction patterns of starting activated mixtures are presented in Fig. 1.

All three mixtures were submitted to the same milling conditions but yet they show some significant differences. X-ray patterns of starting mixtures containing ZnO, TiO_2 -anatase together with an insignificant amount of rutile phase and a small amount of zinc-titanate phase. After 15 minutes of mechanical treatment of ZMTO-0, the intensity of ZnO diffraction peaks decreased compared to ZMTO-1.25 and ZMTO-2.50, while peaks of anatase almost completely disappeared. Intensive disappearance of an ordered crystal structure is an indicator of extremely high transfer of mechanical energy to the powder during mechanical treatment. Also, after 15 minutes of mechanical treatment detectable traces of product Zn_2TiO_4 were present in the ZMTO-0 mixture.

The intensities of all peaks are sharper with increasing the amounts of MgO as an additive. An insignificant traces of a new zinc titanate phase are detectable in ZMTO-1.25 but

not within ZMTO-2.50 mixture.

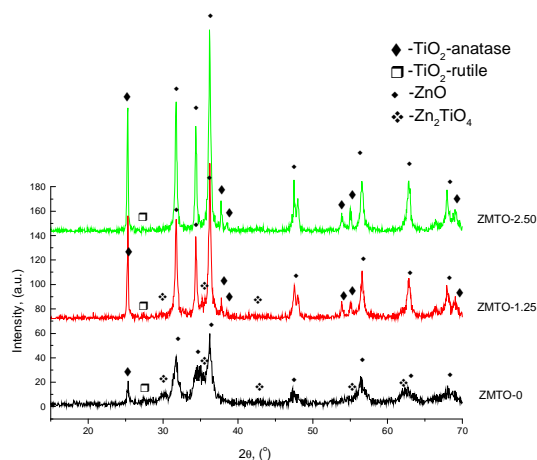


Fig. 1 X-ray diffraction patterns of mechanically activated starting mixtures with different amounts of MgO

That indicates that MgO is very rigid and stable oxide and is situated around ZnO and TiO₂ particles that are brittle and soft compared to MgO particles and therefore represents a barrier for both mechanical treatment and mechanochemical reaction.

The results obtained during compaction under conditions applied are presented in Fig.

2.

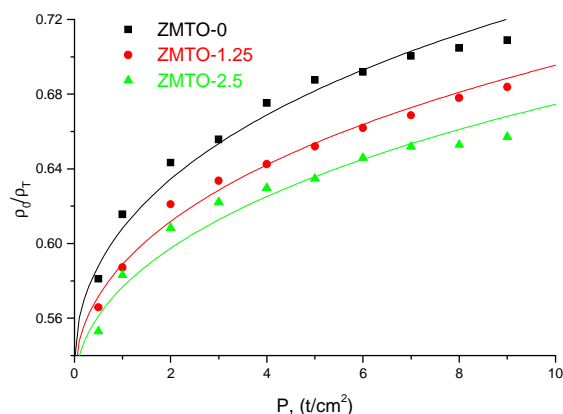


Fig. 2. Ratio of green to theoretical density in dependence on the compaction pressure

In the given pressure interval, the density values decrease with MgO addition. It is important to point out that all powders show similar behavior and follow the same function during the compaction process in spite of completely different phase compositions, as we mentioned before when discussing X-ray diffraction patterns (Fig. 1.).

The specimens pressed under pressures above 4 t/cm² were extremely fragile and thus not convenient for handling. Also, the largest variety in densities occurs until 4t/cm² for all three mixtures, therefore that is the pressure chosen for preparing specimens for sintering process.

The results obtained during the compaction process were fitted with a phenomenological compacting equation proposed by R. Panelli and F. A. Filho [20]:

$$\ln\left(\frac{1}{1-D}\right) = A\sqrt{P} + B \quad (1)$$

where P is the applied pressure, D is the relative density of the compact, A is a parameter related to densification of the compact by plastic deformation, and B is a parameter related to

powder density at the start of compaction. Tab. I presents the values of A and B for all three mixtures. Constants A and B can be used as parameters to characterize the powder behavior during pressing. It can be stated that parameter A (inclination of the compressibility curve) provides the plastic deformation capacity of the powder in compaction.

Tab. I The value of constants characteristics of the powders

sample	A	B
ZMTO-0	0.1687	0.7678
ZMTO-1.25	0.1389	0.7492
ZMTO-2.50	0.1217	0.7378

Thus, as A increases, the powder undergoes increasing plastic deformation during compaction. It is also postulated that parameter B (interception of the curve resulting from Eq. (1) at zero pressure) expresses the density in the absence of pressure. Plastic materials, especially soft metals, possess the highest A values and the brittle materials-lower values, as shown in Tab. I.

In order to investigate thermal behavior of the mixtures and to calculate the activation energy of the reaction, DTA was performed during non-isothermal heating from room temperature to 1100°C with constant heating rates (10, 20 and 30°C/min) in air atmosphere. The DTA curves obtained are shown in Fig. 3. One small endo-peak is noticeable for all three mixtures in the range from 250-270°C probably due to evaporation of some impurities absorbed from the atmosphere. The two noted exothermal effects are a consequence of three processes.

The first exo-peak in the temperature range from 600 to 950°C is the result of the two exo-peaks overlapping: first one is due to arrangement of the crystal structure and crossings of ZnO and TiO₂ cations between normal and inverse spinel [17], the second one is due to nucleation process and spinel formation [20]. The third exo-peak in a range from 950 to 1100°C is the result of crystal growth at higher temperatures [21]. Considering all three peaks are near by, we can conclude that the MgO amount added in the mixtures reduce the sintering temperature slightly.

Kissinger's [22] equation was used in order to determine the activation energy of zinc-titanate formation and the values for mixtures ZMTO-0, ZMTO-1.25 and ZMTO-2.50 are $E_a=182.3$, 224.7 and 325.1 KJmol⁻¹, respectively. The activation energy increases with MgO addition, indicating that higher energy is needed for reaction in the mixture with increased addition of MgO and leads us to conclude that MgO is an obstacle not only for process of mechanical activation but for zinc-titanate formation as well.

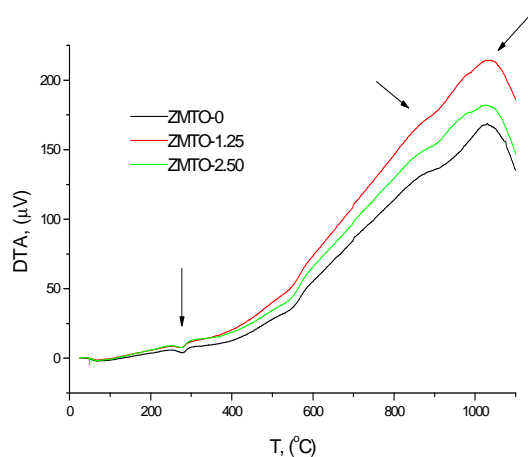


Fig. 3 DTA curves of powder mixtures

Fig. 4. a), b) and c) show densities of Zn_2TiO_4 ceramics with MgO addition (0, 1.25 and 2.50 wt.%) sintered isothermally in air atmosphere at four different temperatures (800, 900 1000 and 1100°C). Green densities were lower with the addition of MgO and were 67.5, 64.2 and 63% of the theoretical density for ZMTO-0, ZMTO-1.25 and ZMTO-2.5 samples, respectively (theoretical densities (TD) = 5.06, 5.03 and 5.01 g/cm^3 for ZMTO-0, ZMTO-1.25 and ZMTO-2.5, respectively). Densities of all three mixtures increased with sintering temperatures reading their maximum of 73% TD for the ZMTO-0 mixture, 75% TD for ZMTO-1.25 and 74.5% TD for ZMTO-2.5 mixture for 1100°C. A minimum change in density was obtained for mixtures sintered at 800 and 900°C and in spite of lowest green density in ZMTO-2.50 mixture, the maximum change in density occurs within the mentioned mixture. So, we can say that increase of MgO addition increases the densification rate, though the resulting densities are very similar.

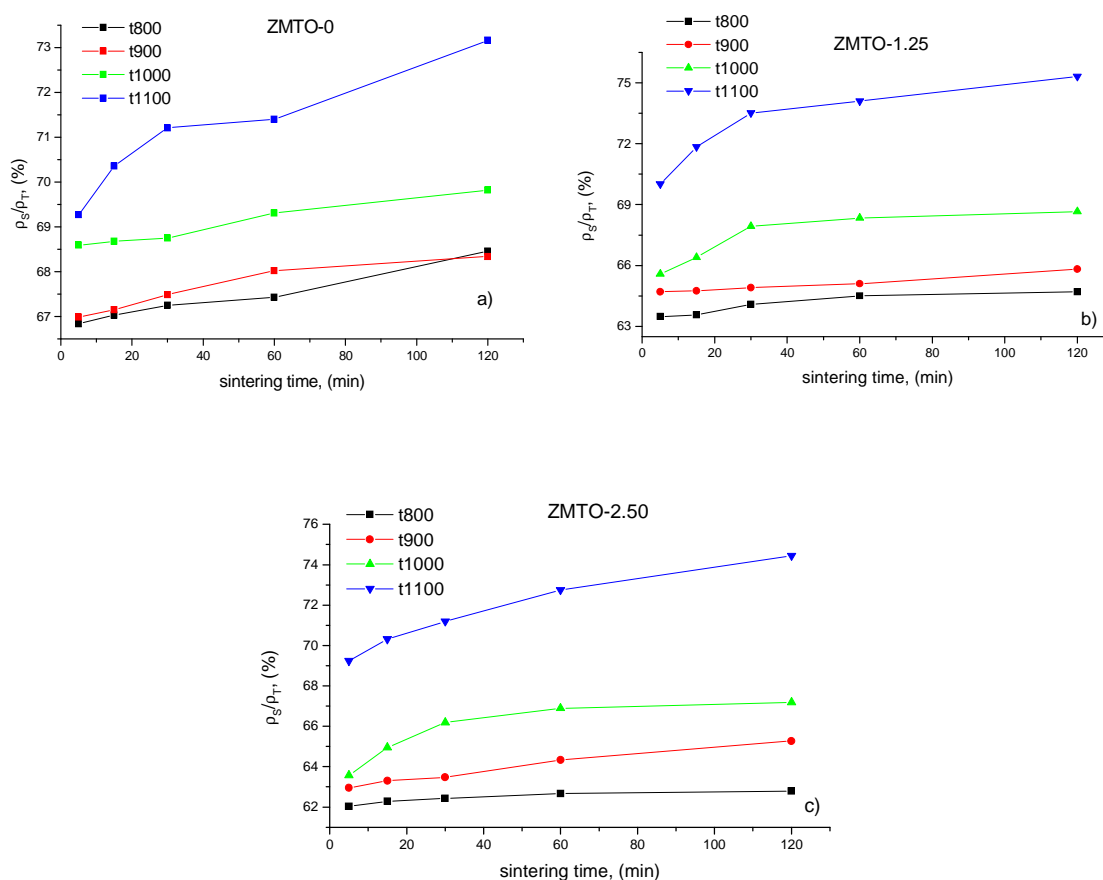


Fig. 4 Densities of Zn_2TiO_4 ceramics with a) 0 wt.% MgO, b) 1.25 wt.% MgO and c) 2.50 wt.% MgO, sintered isothermally at four different temperatures

The kinetics of the sintering process of Zn_2TiO_4 powders with MgO addition (0, 1.25 and 2.50 wt.%) at temperatures of 1000 and 1100°C was analyzed using the phenomenological equation based on the process of transport of activated volume [23].

This equation describes the volume shrinkage of a material during isothermal sintering as:

$$\frac{\Delta V}{V_0} = \frac{K}{1 + C \exp(-st)} \cdot (st)^n \quad (2)$$

where K is the process rate constant, C is a constant defining the ratio between the starting effective activated volume and the equilibrium activated volume, s is a time constant and n is a constant which depends on the process mechanism. Lower sintering temperatures were not analyzed as the shrinkage rate was very low and the process of synthesis of starting powders was still the dominant process.

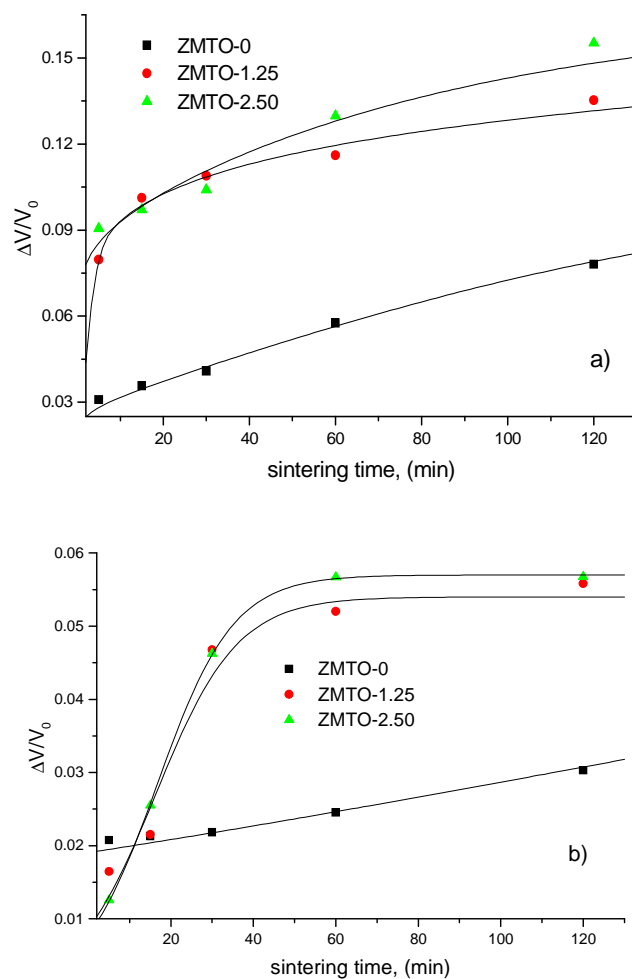


Fig. 5. Zinc-titanate ceramics with MgO addition (0, 1.25 and 2.50 wt.%) sintered isothermally at a) 1100°C and b) 1000°C

Fig. 5. a) and b) shows that good agreement has been obtained for all powders at both sintering temperatures. The process rate constant determined for all analyzed powders was $K=0.089$, 0.07 and 0.146 for Zn₂TiO₄ with 0, 1.25 and 2.50 wt.% MgO addition sintered at 1100°C and $K=0.064$, 0.054 and 0.057 for Zn₂TiO₄ with 0, 1.25 and 2.50 wt.% MgO addition sintered at 1000°C. It is noticeable that this constant is lower for the lower sintering temperature. As only two sintering temperatures were analyzed it was not possible to determine the process activation energy using this parameter. The values of the constant determining the process mechanism were $n=0.10$, 0.14 and 0.08 for Zn₂TiO₄ with 0, 1.25 and 2.50 % MgO addition sintered at 1100°C, while considerably smaller values were obtained for

the lower sintering temperature.

The reciprocal values of this constant can be used to analyze which diffusion mechanism is dominant during the sintering process [24]. In this case all obtained values are well above 2, confirming the dominance of the grain boundary diffusion mechanism.

Conclusions

The phase composition in ZnO-TiO₂ with the addition of MgO = 0-2.50 wt.% solid solutions along with the compaction process, thermal behavior and a detailed analyses of isothermal sintering was studied. The main conclusions are:

- MgO is a very rigid and stable oxide and is situated around ZnO and TiO₂ particles that are brittle and soft compared to MgO particles and therefore obstruct both mechanical treatment and the beginning of the mechanochemical reaction. Activation energies calculated from DTA measurements confirmed our statement.
- The density values of compacts decreased with MgO addition with increase in pressing pressure, although all mixtures follow the same function and can be fitted well with the Panelli and A. Filho's compaction equation,
- Densities of all three mixtures increased with sintering temperatures reaching their maximum at 1100°C, as expected. The proposed mechanism for isothermal sintering is grain boundary diffusion.

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Садржај: Циљ рада је била анализа изотермског синтеровања цинк титанатне керамике допиране магнезијум оксидом. Смеше цинк оксида, титан диоксида и магнезијум оксида (0, 1,25 и 2,50 теж. %MgO) активирани су 15 минута у планетарном млину. Прахови су затим пресовани под различитим притисцима и резултати су фитовани феноменолошком једначином пресовања. Изотермско синтеровање је извођено у атмосфери ваздуха 120 минута на различитим температурама. Структурна карактеризација система ZnO-TiO₂-MgO после млевења извршена је рендгенском дифракционом анализом. Диференцијална термална анализа указала је на различите енергије активације за различите концентрације додатог адитива. Главни закључак је да су веће густине после синтеровања постигнуте са праховима којима је додат магнезијум оксид и да додаток истог стабилнише кристалну структуру цинк титаната.

Кључне речи: Пресовање, Синтеровање, Рендгенска дифракција, Диференцијална термијска анализа, Систем ZnO-TiO₂.
