Structural characterization and electrical properties of sintered magnesium–titanate ceramics

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1. Introduction

Many recent investigations were based on development of materials with low dielectric loss in microwave range, because of their wide usage in modern communication devices, such as cellular telephones, antennas, and global positioning systems [1–4]. From this point of view, low-cost dielectric materials with dielectric constant of 10–20 and low dielectric losses are required. In the binary system of MgO–TiO₂, two magnesium–titanates are mentioned above. These compounds have dielectric constant ε = 16, respectively [5]. Moreover, the influence of the molar ratio of these phases on dielectric constant is registered [6]. The MgTiO₃ geikite (rhombohedra of ilmenite structure with space group R̄3), is formed above 600 °C and it is stable in the range from room temperature to its melting point [7,8]. The Mg₂TiO₄ (cubic of inverse spinel type with space group Fd3m) is formed at temperatures above 1150 °C and undergo a phase transition in the process of cooling at ~1000 °C to a tetragonal modification (space group P4/2mm) [9].

So far, many methods for the preparation of MgTiO₃ and Mg₂TiO₄ were reported in literature, such as thermal decomposition of peroxide precursors, hydrothermal mechano-chemical complication routes, sol–gel routes, auto-ignited method, chemical coprecipitation and metalorganic solution deposition technique [4,10]. The solid-state reaction by grinding in mill is often used method, due to its simplicity, inexpensiveness, applicability, etc. In addition, it is well known that mechanical activation could simplify or accelerate solid-state reaction, reducing temperatures of chemical reaction or sintering temperature [11]. The intention of this work was to determine influence of mechanical treatment on structure of milling mixtures and changes in electrical properties of sintered samples.

2. Experimental procedure

Starting components were MgO (99% Sigma–Aldrich) and TiO₂ powders (99.8% Sigma–Aldrich). Mixtures at a molar ratio MgO:TiO₂ = 2:1 and ball to powder mixture mass ratio 20:1 were mechanically activated in a high energy planetary ball mill device (Retsch type PH 100), with zirconia-oxide vials and balls. Milled pow-
ders have been labeled as MT-\(t\), where \(t\) denoted the time of milling, and MTS-\(t\), for sintered samples. The morphology of obtained powders have been investigated by scanning electron microscopy (JEOL JSM-6390 LV). Textural characteristics of starting MgO:TiO\(_2\) mixture and milled powder, were determined by N\(_2\) physisorption method. Measurements were carried out using a Sorptomatic 1990 Thermo Finnigan at \(-196^\circ\)C temperature after outgassing pretreatment of the samples at 110 \(^\circ\)C for 18 h.

The binder-free powders were compacted using the uniaxial double action pressing process under pressure of 392 MPa in an 8 mm diameter tool (Hydraulic press Ring, P-14, Vebl Thuringer). The compacts were placed in an alumina boat and heated in a tube furnace (Lenton Thermal Design Type 1600) and sintered isothermally at 1300 \(^\circ\)C in air atmosphere for 2 h and the heating rate of 10 \(^\circ\)C min\(^{-1}\). The density of specimens was calculated from the measurements of their diameter, thickness and mass.

The Raman scattering measurements of powders and sintered pellets were performed by a TriVista TR557 triple spectrometer equipped with a nitrogen-cooled CCD detector. The spectra were collected in backscattering micro-Raman configuration using 514 nm line of a mixed Ar\(^+\)/Kr\(^+\) laser with output power 30 mW. Measurements were carried out in the range of 100–1500 cm\(^{-1}\) at room temperature.

The measurements of specific electrical resistivity, capacitance and loss tangent of samples were performed in the frequency range from 20 Hz to 1 MHz with a LCR meter Agilent 4284A, on sintered specimens coated with silver electrodes.

### 3. Results and discussion

There are three different polymorphs of TiO\(_2\) at ambient conditions: body-centered tetragonal structure of anatase (space group \(I_4_1/amd\)), orthorhombic brookite (\(Pbca\)), and tetragonal rutile (\(P4_2/mnm\)). According to the factor group analyses there are six Raman active modes in anatase (\(A_{1g} + 2B_{1g} + 3E_g\)) [12], four Raman active modes in rutile (\(A_{1g} + B_{1g} + B_{2g} + E_g\)) [13], whereas 36 vibrational bands are predicted in brookite phase [14]. Besides, TiO\(_2\) has two

<table>
<thead>
<tr>
<th>Sample</th>
<th>Position and assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT-0</td>
<td>143 196 396 515 637</td>
</tr>
<tr>
<td>MT-5</td>
<td>142 196 314 361 515 638</td>
</tr>
<tr>
<td>MT-10</td>
<td>142 196 314 338 360 396 425 447 514 637</td>
</tr>
<tr>
<td>MT-20</td>
<td>142 197 315 338 359 396 425 448 518 637</td>
</tr>
<tr>
<td>MT-40</td>
<td>142 197 267 287 310 315 339 357 397 425 448 514 525 576 637</td>
</tr>
<tr>
<td>MT-80</td>
<td>142 198 270 287 312 315 339 355 397 414 426 446 522 574 606 637</td>
</tr>
<tr>
<td>MT-120</td>
<td>142 199 271 287 312 315 338 356 362 398 415 428 448 523 568 574 605 637</td>
</tr>
</tbody>
</table>

- anatase, -TiO\(_2\) II, - srilankite, - rutile
high-pressure phases: TiO$_2$ II with orthorhombic structure (space group $Pbcn$), and monoclinic srilankite ($P 2_1/c$) [15]. At the pressure higher than 2.56 GPa, TiO$_2$ II is irreversibly formed from anatase and rutile [16]. On the other side, MgO, as a cubic crystal with inversion symmetry, has no first-order Raman active modes [17].

The Raman spectra of non-milled powders and those milled for different time intervals in the range of 100–800 cm$^{-1}$ are shown in Fig. 1. All Raman modes in the spectra of non-milled powder can be assigned to the Raman active modes of anatase crystal [12] as follows: 143 cm$^{-1}$ (E$_g$(1)), 196 cm$^{-1}$ (E$_g$(2)), 396 cm$^{-1}$ (B$_1g$(1)), 515 cm$^{-1}$ (combination of A$_1g$ and B$_1g$(2) that cannot be resolved at room temperature [18]) and 637 cm$^{-1}$ (E$_g$(3)). The anatase modes are dominant in Raman spectra of all activated powders, although their intensities decrease and widths increase as the time of activation extended.

In addition to anatase modes, barely noticeable a few new bands between 300 and 400 cm$^{-1}$ in Raman spectra of MT-5 quite visible in MT-10 spectra, can be assigned to TiO$_2$ II phase [16]. In the Raman spectra of the powders activated for more than 80 min, the weak shoulders, which can be assigned to srilankite and rutile phases [16,19], are also present. The position of all observed Raman modes obtained by deconvolution of the Raman spectra into a series of separated Lorentzian shape peaks using last–squares optimization method, as well as their assignations, are summarized in the Table 1. As it can be seen, there are no significant shifts in the bend positions. Small blue shifts with extended activation time, noticed for the E$_g$(2) anatase mode at $\sim$196 cm$^{-1}$ and TiO$_2$ II modes at $\sim$170 and $\sim$267 cm$^{-1}$, most probably are the consequence of the variation in crystal position of oxygen atoms, as well as increased nonstoichiometry and lattice strain introduced by mechanical treatment.

### Table 2

Results obtained by N$_2$ sorption.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{tot}$ (cm$^3$/g)</th>
<th>$V_{mes}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT-0</td>
<td>15.8</td>
<td>0.051</td>
<td>0.047</td>
</tr>
<tr>
<td>MT-5</td>
<td>10.4</td>
<td>0.038</td>
<td>0.033</td>
</tr>
<tr>
<td>MT-10</td>
<td>7.7</td>
<td>0.026</td>
<td>0.024</td>
</tr>
<tr>
<td>MT-20</td>
<td>6.4</td>
<td>0.034</td>
<td>0.037</td>
</tr>
<tr>
<td>MT-40</td>
<td>5.5</td>
<td>0.029</td>
<td>0.031</td>
</tr>
<tr>
<td>MT-80</td>
<td>7.8</td>
<td>0.033</td>
<td>0.034</td>
</tr>
<tr>
<td>MT-120</td>
<td>9.2</td>
<td>0.048</td>
<td>0.054</td>
</tr>
</tbody>
</table>

![Fig. 3](#)

![Fig. 4](#)
For more detailed investigation of the structural changes due to mechanical activation, Raman mode of anatase at \( \text{C}_2 \text{g} \) \( 142 \) (E\(_g\)(1)) and TiO\(_2\) II mode at \( \text{C}_2 \text{g} \) \( 338 \) cm\(^{-1}\) are particularly analyzed [19]. In the Fig. 2 full width at half maximum (FWHM) is shown for modes mentioned above as a function of milling time. A growth of \( \text{E}_g\)(1) linewidth for the period of activation longer then 5 min (Fig. 2(a)), together with the decrease in the intensity and broadening of all anatase modes (Fig. 1) can be explained by fragmentation of anatase grains and introducing defects during treatments. Note also that the appearance of new TiO\(_2\) phases, srilankite and rutile (which according to the literature have Raman modes at about 151 cm\(^{-1}\) [15] and \( \sim 143 \) cm\(^{-1}\) [13], respectively), can influence the broadening of the Raman feature at \( \sim 142 \) in the powders activated for more than 40 min. On the other hand, mode of TiO\(_2\) II (Fig. 2(b)) exhibits completely different trend: FWHM of this mode decreases with activation time for the treatment shorter than 80 min, but starts to increase for longer activation time. Such behavior points out not only to formation and gradual ordering of TiO\(_2\) II phase at the beginning of activation, but also to the fragmentation and disorder of this phase that begins after 80 min of milling.

The nitrogen sorption isotherms are very similar shape for all samples. According to the IUPAC recommendation for classification of adsorption isotherms, obtained isotherms are corresponding to Type II isotherms, whereas the hysteresis loops can be classified as Type H1 [20]. Nitrogen adsorption/desorption isotherms for sample MT-0 and MT-120 are presented in Fig. 3.

The results obtained by \( \text{N}_2 \) sorption measurements are summarized in Table 2. An unusual behavior may be noticed: specific surface area, as well as total pore volume, decreases with milling time, reaching minimum values of 5.5 m\(^2\)/g and 0.029 cm\(^3\)/g respectively, and after 80 min starts to increase. There are few possible reasons which can contribute to the reduce of specific surface area (SSA) for approximately 65%. An irregular morphology of MgO can be observed in SEM micrograph of MT-0, whereas TiO\(_2\) has smaller spherical particles (Fig. 4). The decrease in BET surface area may be associated to the agglomeration of small unstable TiO\(_2\) particles. The irregular morphology of MgO was broken during the milling process and the pore structure destructed [21,22], which could also lead to decrease in SSA owing to cold welding of MgO attired particles. Furthermore, the reason for unexpected behavior of SSA can be related to the disappearance of anatase and appearance of new phase of TiO\(_2\) II (Fig. 2(b)), having lower SSA than starting oxides. After 40 min of activation, the new phase starts to create in the form of larger particles produces greater SSA. Due to longer time of milling treatment these particle start to behave like the mechanical activation and fragmentation is at the beginning.

The microstructure analyses of MgO–TiO\(_2\) system have showed that the initial MgO powder consisted of irregularly shaped agglomerates with a size of 2 microns approximately and spherical particles TiO\(_2\) with size of 150 nm. For the activated samples, formation of soft agglomerates has been noticed as a formation of new phase, because of mechanically induced particles deforma-
tion, which is in agreement with Raman spectroscopy. The micrograph of the sample MT-80 indicates particle fragmentation.

The Raman spectra of the samples obtained by sintering non-milled and milled powders at 1300 °C are shown in Fig. 5. During the treatment at a higher temperature, two phased sistem [MgTiO$_3$ and Mg$_2$TiO$_4$] is formed [23]. According to the factor group analyses, MgTiO$_3$ there are ten Raman active modes 5A$_g$ +5E$_g$, whereas spinel Mg$_2$TiO$_4$ has five ones (A$_{1g}$ + E$_g$ +3F$_{2g}$). All ten bends corresponding to MgTiO$_3$ were observed in the Raman spectra of sintered samples at the following position: 225 cm$^{-1}$ (A$_g$), 282 cm$^{-1}$ (E$_g$), 307 cm$^{-1}$ (A$_g$), 353 cm$^{-1}$ (E$_g$), 398 cm$^{-1}$ (E$_g$), 485 cm$^{-1}$ (E$_g$), 504 cm$^{-1}$ (A$_g$), 638 cm$^{-1}$ (E$_g$), ~725 cm$^{-1}$ (A$_g$) [24,25]. On the other hand, it is hard to resolve the Raman modes that originated from Mg$_2$TiO$_4$ phase, as they are at the similar positions as the modes of MgTiO$_3$ and partially overlapped with them [26]. Besides, an additional Raman feature, noticed at 596 cm$^{-1}$, is assigned to MgTiO$_3$ II. These high-pressure MgTiO$_3$ phase with the lithium-neonate structure may be metastable quench phase of perovskite [8].

As it can be seen from Fig. 5(a), all Raman spectra of sintered samples are almost identical, considering the number and position of the main features. The only difference observed is in the relative intensity and shape of some features, and special attention is dedicated to the analysis of the Raman feature at about 720 cm$^{-1}$. Deconvolution of this feature by two separated Lorentzian shape peaks using last–squares optimization method for sintered samples is shown in Fig. 5(b). The positions of these peaks in all spectra are at ~713 and ~730 cm$^{-1}$, but their intensity ratio varies. First of these peaks at ~713 cm$^{-1}$ can be Raman mode ascribed to the vibrations of O atoms in TiO$_6$ octahedrons of ordered MgTiO$_3$ structure [27]. The appearance of the mode at ~730 cm$^{-1}$ indicates the presence of structural order–disorder at short-range, suggesting the presence of [TiO$_6$] complex clusters and defects (oxygen vacancies) introduced by mechanical activation and subsequent sintering [27]. Note that [TiO$_6$] and [TiO$_5$] complex clusters in the sintered samples studied here can also belong to the Mg$_2$TiO$_4$ structure. So, the intensity ratio of the Raman features at ~713 and ~730 cm$^{-1}$, presented in Fig. 5(c), can be use as an indicator of structural ordering and concentration of oxygen vacancies. This indicates that mechanical activation before sintering can decrease the concentration of oxygen vacancies into the lattice, resulting in a more ordered structure of sintered samples. However, the activation is able to increase the degree of structural order into the lattice just for shorter activation time (up to 80 min), whereas extension of this process is associated with structural disorder.

Values of electrical measurements, dielectric permittivity ($\varepsilon_r$), loss tangent (tg$\delta$) and specific resistance ($\rho$, given in Ωcm) as well as densities obtained after sintering (d, given in percents of theoretical density) as a function of time of mechanical treatment are given in Table 3. The resultes pointed out that the dielectric permittivity of these specimens increase with activation time. Also it is known from the literature data that different ratio between phases has influence in $\varepsilon_r$ values [6]. It is believed that the densities play an important role in controlling dielectric loss. The tg$\delta$ value is generally affected not only by the lattice vibration modes, but also by the pores, the second phases, the impurities, the lattice defect, crystallizability and inner stress [28]. The increase in activation time is beneficial to the densification after sintering and crystallizability until the loss tangent value reaches the minimum. The further increase in activation time is result in the appearance of abnormal grains and pores after sintering process and consequently leads to the increase of the tg$\delta$ value [29]. Specific resistance increase with milling time until 80 min is probably induced with existence large crack between areas. Sample MT-

![Fig. 6. SEM micrographs of samples (a) MT-0–1300, (b) MT-20–1300, (c) MT-80–1300 and (d) MT-120–1300.](image-url)
120–1300 has more compact structure and consequently lower values of specific resistance.

Micrographs of samples sintered at 1300 °C for 2 h indicate medium sintering stage along with enclosed but not spherical pores and two different phases, Fig. 6, which is in accordance with results obtained with Raman spectroscopy. Presence of fracture between grains, which is due to presence of agglomerates in starting powders, was noticed. Observing morphology of MT-120–1300, may be noted that it is the most homogeneous structure, which cause the higher values of dielectric constant.

4. Conclusion

In this article the influence of ball milling process on the structure of MgO–TiO2 system, along with its influence on electrical properties of post-sintering samples was investigated. The Raman spectroscopy of activated powers pointed out phase transition of anatase, through high pressure TiO2 II and srilankite, to the most stable rutile phase. In addition, the mechanical strain have led to improvement the structural and electrical properties of sintered magnesium-titanate ceramics.

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References