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# Influence of Mechanical Activation on Synthesis and Properties of the MgO-$TiO_2$ System

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***Abstract:***

*Materials applied in electronics such as multilayer capacitors are an important field of ceramic materials. Magnesium titanate based dielectric materials are used for producing type-I capacitors. A common way of obtaining this material is a solid-state reaction during reaction sintering. The process of sintering can be enhanced if mechanical activation precedes. In this work starting powders of magnesium carbonate ($MgCO_3$) and titanium dioxide ($TiO_2$) with a rutile crystal modification were weighed to attain a 1:1 molar $MgCO_3$:$TiO_2$ ratio. Mechanical activation of the starting mixture was performed by high energy ball milling using ZrO balls and vessels with a ball to powder mass ratio of 40:1. The observed grinding times were 15, 30, 60 and 120 minutes. Powder characterization was conducted using X ray powder diffraction, DTA analysis up to 1000$^oC$ and particle morphology changes were observed with Scanning Electron Microscopy. Isothermal sintering of compacted powders was conducted at 1100$^oC$ during 30, 60 and 180 minutes. For specimens synthesized in such a manner, microwave dielectric properties were measured, quality factor Q, specific electrical resistivity ($\rho$) and the dielectric constant ($\varepsilon_r$). In this work we explain the influence of mechanical activation on the $MgCO_3$-$TiO_2$ system leading to titanate formation during sintering, as well as induced changes in microwave dielectric properties.*

***Keywords:*** *Sintering, MgO, $TiO_2$, Dielectric constant, Quality factor, Specific electrical resistivity .*

## Introduction

Ceramic materials have been in use in many different areas of human wellbeing for a very long time. Materials applied in electronics are important fields of ceramic materials. Low permittivity and high-*Q* dielectric ceramics have recently become of great importance, since ceramic substrates should have a low permittivity for the application of advanced substrate materials needed for microwave integrated circuits. Based on the silicate group there are many other materials e.g. titanates which are not routinely used yet for plasma spraying.

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Titanates in general, represent a wide and important group of technical ceramics. Perovskites $A^*TiO_3$ are interesting members of this group. They can be face-centered cubic ($A^*$= Ca, Ba, Sr) or trigonal ($A^*$= Fe, Co, Ni, Mn, Mg) depending on the chemical composition. Magnesium titanate ($MgTiO_3$) is well known as dielectric materials based on it are classically used in the production of type-I ceramic multilayer capacitors [1]. $MgTiO_3$ is a low loss dielectric ceramics and has important applications in microwave communication systems. The former has a dielectric constant of 170 with a negative temperature coefficient and the latter has a dielectric constant of 17 with a positive temperature coefficient [2]. Recent development of microwave communication systems requires materials that can be used at microwave frequencies as resonators in filters or oscillators in radar detectors, cellular telephones and global positioning satellite devices. During the last two decades there has been a growth of interest for preparation and characterization of low-loss dielectrics suitable for such engineering applications. Most of the ceramics exploited for communication applications have temperature-stable dielectric properties with relative permittivities in the range 20-90, and *Qf* products (where *Q* is the quality factor and *f* frequency in GHz) in the range 5000-400000. $MgTiO_3$ is one such promising material. Magnesium titanate also melts congruently in the temperature 1732 / 1835 $^oC$. The mineral giekielite $MgTiO_3$, exists in nature, and has many industrial applications, in dew sensors, in pigments for protective coatings, with good water, weathering and impact resistance, in the composition of binders by increasing the flexural in chip capacitors, high frequency capacitors and temperature compensating capacitors [3].

## Experimental

In this work starting powders of magnesium carbonate ($MgCO_3$) and titanium dioxide ($TiO_2$) with a rutile crystal modification were measured to attain the molar ratio of $MgCO_3$:$TiO_2$ = 1:1. Mechanical activation of the starting mixture was performed by grinding in a high energy mill in a planetary ball mill device (Fritsch Pulverisette 5) with ZrO balls and vessels where the ball to powder mass ratio was 40:1. The grinding times were 15, 30, 60 and 120 minutes. Depending on the grinding time, four mixtures were used in our work (for 15 (MT15), 30 (MT30), 60 (MT60) and 120 minutes (MT120)) and one non-activated mixture (MT00).

The relative shrinkage of samples in order to investigate the reactive sintering process was followed by a sensitive dilatometer Bähr Gerätebau GmbH Type 702s. Heating was carried out in air with a constant heating rate of 20 °C/min, from room temperature to 1000 °C.

Micrographs were taken with a scanning electron microscope JSM-6460 LV JEOL with an energy depressive X ray spectroscopy unit EDS INCA x-sight Oxford Instruments.
Preparation of samples for sintering was performed by pressing the prepared powder mixtures in a VEBTHURINGER INDUSTRIEWERK REUENSTEIN dual hydraulic press, with a pressure of 400 MPa. The samples obtained were non-isothermally sintered up till 1100 $^oC$ and then isothermally at that temperature for different times (0, 30, 60 and 180 minutes).
After three hours of sintering at the temperature of 1100$^o$ sample MT-120 had the highest density of 3.72 g/cm$^3$. This represents 93% of the theoretical density.

Measurement of electrical properties of sintered samples in dependence of the frequency was performed on a HIOKI 3532-50 LCR HiTESTER device. In this paper the influence of mechanical activation on individual electric properties is presented based on the measurements and calculations performed.

## Results and discussion

Dilatometric analysis, given on fig. 1, confirms the results obtained by X ray difractometry and thermal analysis [4]. The non-activated mixture shows dimension fluctuations at about 400°C corresponding with mass loss, confirmed with DTA analysis, that originate from carbon dioxide release. All specimens mechanically activated did not show such curve deflection, indicating that carbon dioxide release is enhanced and causes no sudden shape changes of the specimen. During sintering the slope of dilatometric measurements indicates a phase transition at 850°C from $MgTi_2O_5$ to $Mg_2TiO_4$.

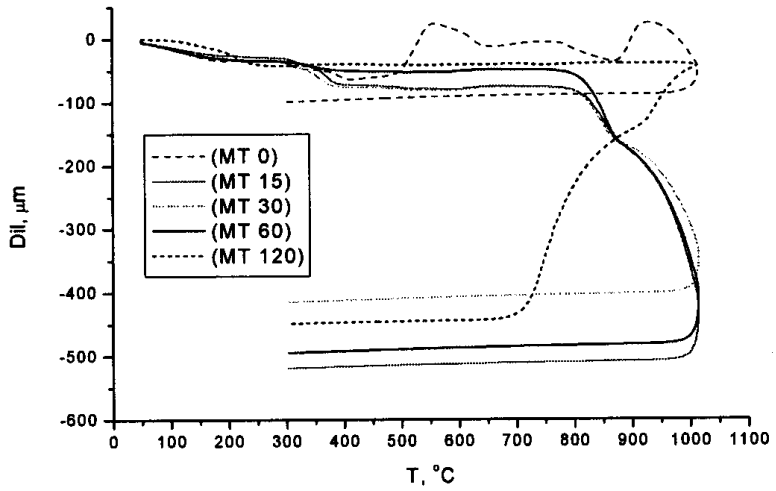


**Fig. 1** Dilatometric analysis

Micrographs on fig. 2 and 3 represent powder morphology, breakage structure on the green body and sintered specimen breakage for specimen MT0 of the non-activated mixture and for the powder activated 60 minutes, MT60. The non-activated mixture shows two different phases and particle shapes due to the existence of starting oxides. Due to pressure applied during compaction we can notice densification caused by rearrangement of powder particles during packing from the green body micrographs. Rod shaped particles formed from a new phase during sintering are visible on fig. 3.

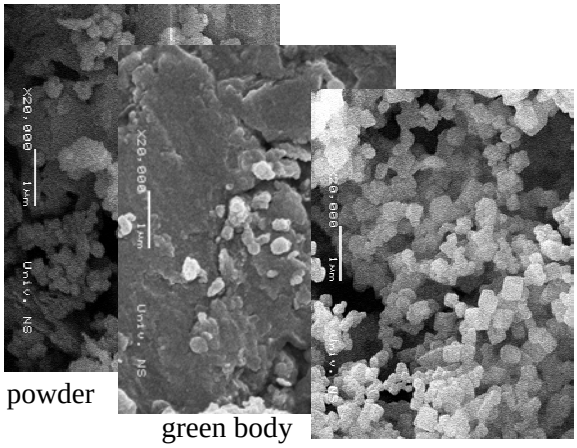


**Fig. 2** SEM of MT0 powders, green body and sample sintered 1000 °C

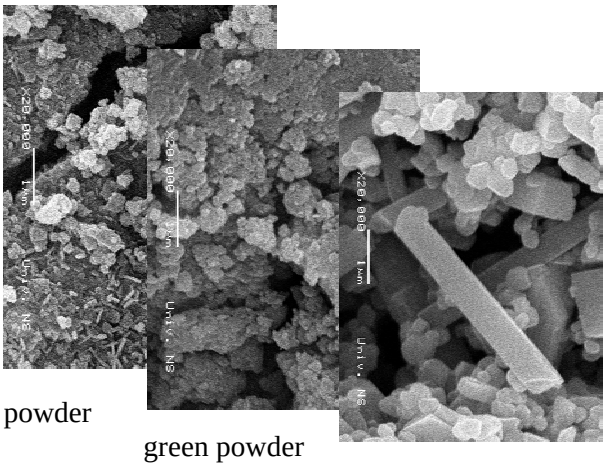


**Fig. 3** SEM of MT60 powders, green body and sample sintered at 1000 °C

Measurement results shown in fig. 4 indicate growth of the quality factor with increased sintering time for activated samples. It also shows changes of the quality factor with increased time of mechanical activation.

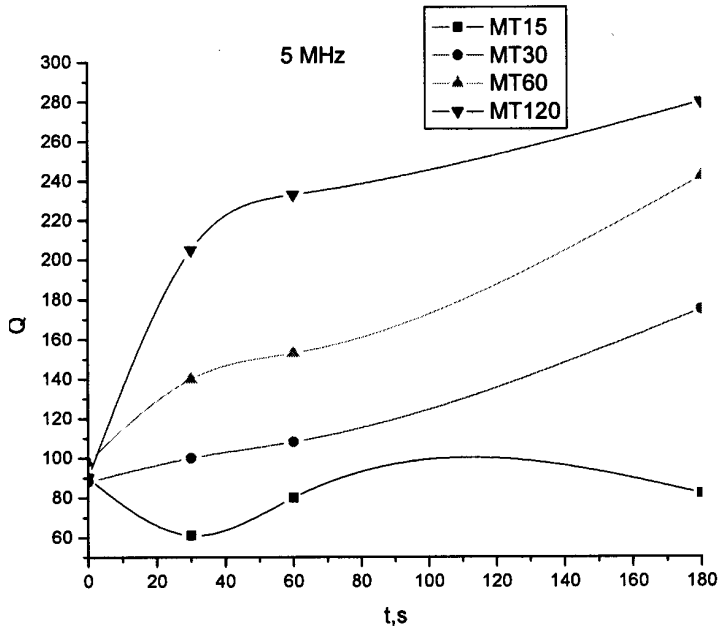


**Fig. 4** Dependence of the quality factor Q on the sintering time for samples sintered at 1100$^{o}$C at 5 MHz

The results obtained from quality factor measurements indicate that synthesis parameters have a great influence on this electrical property of a sintered MgO-$TiO_2$ system. Longer sintering times in combination with longer duration of mechanical activation give a material with an increased quality factor.

Variation of the synthesis parameters can give a material with properties defined in advance. Concretely, the example of the relative dielectric constant shows that varying the sintering time for the same duration of mechanical activation enables selection of a determined value of $\varepsilon_r$. Fig. 5 gives this dependence at the highest measurement frequency of

5 MHz, where graph T0 denotes a sample sintered for 0 minutes at 1100°C, T30 for a sample sintered 30 minutes, T60 60 minutes and T180 denotes a sample sintered for 180 minutes.

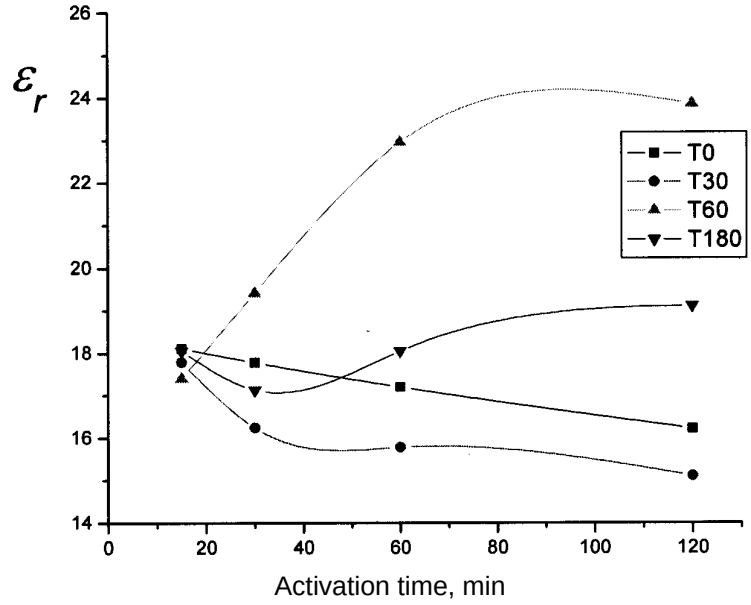


**Fig. 5.** $\varepsilon_r$ for samples measured at 5 MHz

Measurement results show that with increasing duration of the sintering process constant electric dipoles in $MgTiO_3$ change polarization that has a direct influence on the relative dielectric constant. The lowest value for $\varepsilon_r$ is obtained for sample MT120 sintered for 30 minutes. MT60 also sintered 30 minutes has a similar value. These measurement results show that if one wants a material with a high $\varepsilon_r$ value synthesis parameters should be set so that mechanical activation lasts 120 minutes and the sintering time 60 minutes.

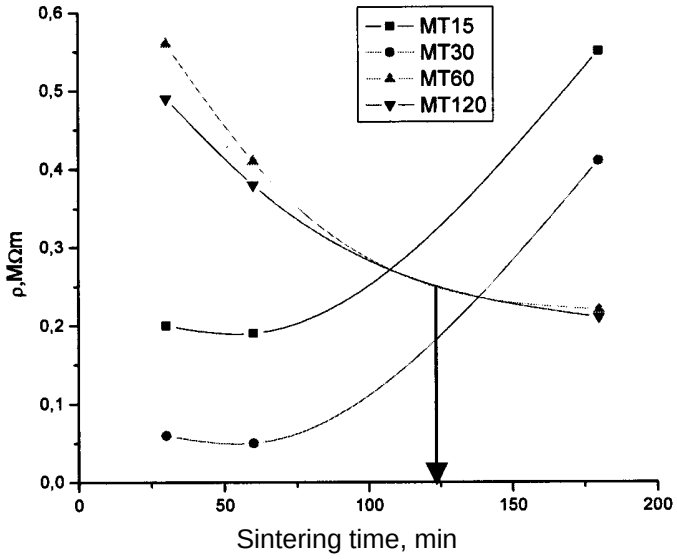


**Fig. 6** Specific electric resitivity $\boldsymbol{\rho}$ as a function of the sintering time

Fig. 6 shows graphs of the dependence of electric resistivity on the sintering time for all activated samples. These results undoubtedly show that samples MT60 and MT 120

behave in accordance with the theory and that the parameter of increased sintering time adequately corresponds to the increase in the sintering temperature. As all experiments were conducted at a constant sintering temperature of 1100°C duration of the sintering process was used as the synthesis parameter.

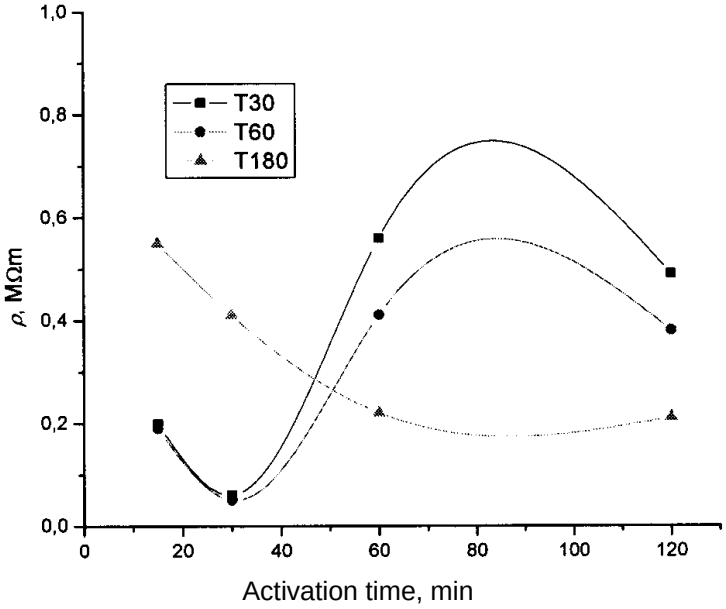


**Fig. 7** Specific electric resitivity $\rho$ as a function of the activation time

The measurement results of specific electrical resistivity confirm the justification of using mechanical activation and indicate that MT 60 and MT 120 are the samples with the best properties. If the sintering time is extended as shown in fig. 7 it can be noted that all samples behave in accordance with theoretical expectations. The optimal sintering time is 120 minutes as further lengthening does not result in significant improvements.

## Conclusions

With increased activation time the reaction occurs at lower temperatures compared to non-activated samples. During mechanical activation basic changes in the material relate to physico-chemical surface parameters and thus changes in the materials reactivity occur. Reduction in the material size leads to increased specific surfaces and thus its reactive capability. Thus, grinding of $MgCO_3$ and $TiO_2$ powders increases their reactivity and enhances the solid state reaction. All analyses indicate that increased grinding times lowers the phase formation temperature and thus shortens the duration of the sintering process.

One of the parameter placed before synthesis of new materials is the time in which they are obtained and in accordance with this the energy put in. Optimal duration of mechanical activation leads to reduced energy consumption and thus reduction of the sintering temperature and shortening of the sintering time. The conclusion can also be reached that the duration of the sintering process has the smallest influence on the non-activated sample. This is confirmed by theoretical assumptions and justifies the use of mechanical activation.

Extension of the sintering time in combination with lengthening the time of mechanical activation gives a material with an increased quality factor. Depending on the needs, variation of synthesis parameters can give exact values of the relative dielectric

constant. Measurement results of specific electrical resistivity also confirm justifiability of mechanical activation and show that samples MT 60 and MT 120 have the best properties.
Based on the results presented in this paper conditions for structure control of magnesium titanate through synthesis parameters have been created. This enables obtaining of materials with properties defined in advance that can be widely applied in the field of electronics.

## References

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***Садржај:*** *Важно место у керамичким материјалима заузимају материјали примењени у електроници, рецимо за израду вишеслојних кондензатора. Магнезијум титанат је базични диелектрични материјал који се користи за израду кондензатора типа I. Уобичајени начин добијања овог материјала је путем синтеровања. Процес синтеровања је у многоме квалитетнији уколико се користи механичка активација. У овом раду као полазни прахови коришћени са магнезијум карбонат ($MgCO_3$) и титан диоксид( $TiO_2$), кристална модификација рурил, где је моларни однос $MgCO_3 : TiO_2$= 1:1. Еквимолска смеша полазних прахова механички је активирана млевењем у високо енергетском планетарном млину са куглама (Fritsch Pulverisette 5) са цирконијум - оксидним куглама и масеним односом кугли и праха 40:1. У зависности од времена млевења у овом раду употребљено је укупно пет смеша, (неактивирана смеша и четири смеше различито временски активиране – 15 минута, 30 минута, 60 минута и 120 минута). Карактеризација прахова је урађена путем X- rey анализе и преко DTA анализе на 1000°C, а морфологија промене прахова праћена је путем Скенирајуће електронске микроскопије. Изотермско синтеровање пресованих узорака рађено је на 1100°C у временским интервалима од 30, 60 и 180 минута. Овако синтерованим узорцима мерена су микроталасна електрична својства, као што су фактор доброте (Q), специфична електрична отпорност (ρ) и диелектрична константа($\varepsilon_r$). У овом раду приказан је утицај механичке активације на синтеровани систем $MgCO_3$ -$TiO_2$ , и промену његових микроталасних диелектричних својстава.*
***Кључне речи:*** *Синтеровање, MgO, $TiO_2$, диелектрична константа, фактор доброте, специфична електрична отпорност.*