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# Effect of Syntesis and Frequency on Electrical Properties on Dielectric Ceramics $MgCO_3$-$TiO_2$

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## I. Introduction

Ceramic materials with functional electric properties hold an important place among new materials. These materials are obtained by sintering through particle interaction during heating of a dispersive mixture of crystal and non-crystal materials. Qualitative and quantitative changes occur at powder particle contacts. Ceramic materials thus attain certain mechanical and electrical properties as a consequence of physical-chemical, structural and microstructural transformations of the material. Rapid development of electronics is lately linked with development and improvement of new components based on titanate, stannate and zirconate ceramics. These ceramic systems belong to the perovskite group of materials. The subject of research in this paper is the MgO-$TiO_2$ system, i.e. magnesium-titanate ($MgTiO_3$).

Modern technologies most often prepare powders for the synthesis of new materials applying mechanical activation – intensive transfer of mechanical energy to powder in specially constructed mechanic activators. Mechanical activation leads to controlled reduction of order and material destruction. As the reaction capability of a material is the consequence of structural properties, reduction of order and destruction in a material occurring during mechanical activation of the powder later causes acceleration of the synthesis process and sintering of a material using activated powder [1]. Besides increasing powder reaction capability mechanical activation can also achieve phase structural transformation.

The market for electronic devices requires faster development and application of new materials with defined properties. Rapid development of electronics has lately depended on development and advancement of new components based on titanate ceramics. Magnesium titanate ($MgTiO_3$) is a basic dielectric material used for the production of type-I condensers [2]. Magnesium titanate is widely applied in industry [3, 4, 5]. Due to its good electric properties magnesium titanate has lately been widely applied in microwave frequency resonators and filter and oscillator antennae for application in communication systems and GPS devices [6].

The dielectric characteristics required for microwave resonator are high dielectric constant ($\varepsilon_r$) to reduce the size of resonators and high quality factor (Q) for achieving prominent frequency selectivity and stability [7]. Moreover, low-sintering temperature is also required to match with low-loss and low-melting point conductors in fabrication of dielectric devices [8]. There are several methods used for reducing sintering temperature of dielectric ceramics such as addition of a low-softening glass or liquid phase sintering aid, chemical pre-treatment and processing of precursor ceramic powders and reduction of particle sizes of starting materials. $MgCO_3$-$TiO_2$ (hereafter referred to as MT) ceramics is well known as the material for temperature compensating capacitor and dielectric resonator. However, it required sintering temperatures as high as 1300ºC.

### *a) Experimental*

Samples were prepared by conventional solid-state ceramic processing using $MgCO_3$ (99.9% p.a.) and $TiO_2$ (99.9% p.a.) as the starting materials. Appropriate amounts of the compositional constituents, those correspondents to the demanded stoichiometric ratio 1:1 were weight out. The powders were submitted to mechanochemical treatment, in a planetary ball mill

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device (Fritsch Pulverisette 5), with zirconium oxide balls (approx. 10 mm in diameter) and the ball to powder mixture mass ratio was 40:1. The time of milling was varied from 15 to 120 min and mixtures, as appropriate samples, were denoted according to the applied time of activation as MT-00, MT-15, MT-30, MT-60 and MT-120. Powders were then sieved through a 0.2 mm sieve.

The binder-free powders were compacted at 400 MPa pressure using the uniaxial double action pressing process in an 8 mm diameter tool (Hydraulic press RING, P-14, VEB THURINGER). Compacts were places in an alumna boat and heated in tube furnace (Lenton Thermal Design Typ 1600). The heating rate was 10°C/min and when the temperature of the furnace reached 1100°C, compacts were sintered isothermally in air atmosphere for 180 min. The density of specimens was calculated from precise measurements of specimen's diameter, thickness and mass.

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.

X-ray powder diffraction patterns of the milled powder mixtures, as well as sintered samples, were obtained using a Philips-Analitical PW-1710 diffractometer, with a $CuK_\alpha$ radiation and a step scan mode of 0.02°/2 s.

Scanning electron microscopy was used to record starting powders MT-00, MT-15, MT-30, MT-60 and MT-120 on a JSM-6460 LV JEOL device with INCA x-sight Oxford analysis EDS analysis.

The measurements of electrical resistivity, capacitance and loss tangent of samples were measured in the frequency range from 500 Hz to 5 MHz frequencies with a HIOKI 3532-50 LCR HiTESTER device at a constant voltage mode (amplitude 0.5 V of sinusoidal signal applied to the specimens). The "four-probe" configuration has been employed. The samples were prepared by painting silver electrodes on both sides following with thermal treatment at 120°C for 2 h performed in order to improve the paint conductivity.

## II. Results and Discussion

Research and analysis of dielectric ceramics has been done for some time so new research is essentially focused on analyzing fine interactions in the synthesis-structure-properties relationship. As in this research the starting components have been greatly influenced (mechanical activation of the powder mixture has a significant influence on the structure of components reacting during the sintering process) it is of great significance to establish the influence of synthesis and structure of the electronic ceramics on functional properties of the electronic components. In this work special attention has been paid to the influence of mechanical activation of 120 minutes on the structure and properties of sintered magnesium titanate. The sintering time was varied from 0 to 180 minutes. In this work special attention has been paid to the influence of mechanical activation and sintering time concerning to electrical properties meassured via different frequencies.

According to our X-ray analysis [9], intensive milling of $MgCO_3$-$TiO_2$ powder mixture leads to the decrease of crystallinity, occurring as a consequence of defect formation and diminution of crystallite size. The diffractograms obtained after 15 and 30 min of activation, show that the decomposition of $MgCO_3$ takes place along with the simultaneous formation of $MgTiO_3$ phase, occurring as a consequence of a solid-state reaction between MgO and $TiO_2$.

We have noticed that: intensities of all starting phases are significantly lowered after 15 min of mechanical treatment, the first significant appearance of a new magnesium-titanate phase along with all the starting phases is established to be after 30 min of mechanical treatment. Microstructure parameters revealed from an approximation method [10] of ball-milled $MgCO_3$-$TiO_2$ powder mixture: particle size ($D_{hkl}$), density of dislocations ($\rho_D$) and lattice strain ($e_{hkl}$) are presented in Figure 1. After sintering, a magnesium-titanate ($MgTiO_3$) phase along with small amounts of unreacted $TiO_2$ [5] phase is observed, Figure 2. Also, phase identification has been done using JCPDS cards 01-079-0831 and 01-074-1940 for magnesium-titanate and titan-dioxide, respectively.

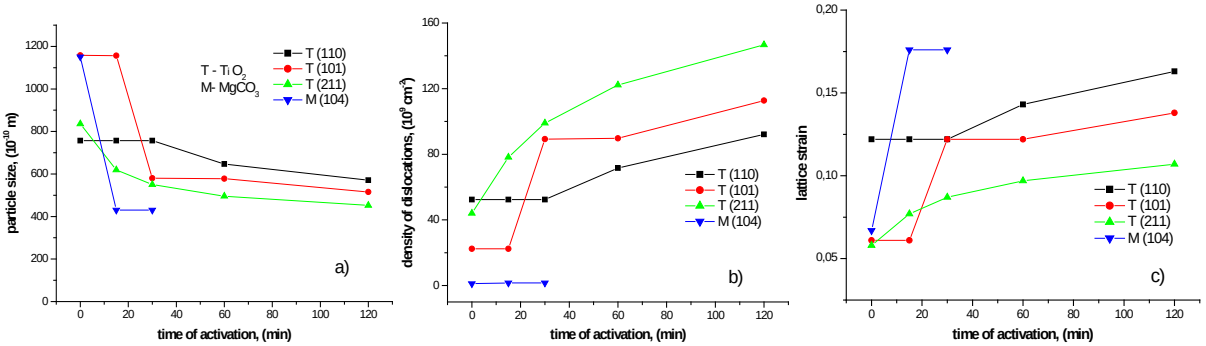


*Figure 1 :* Microstructure parameters: particle size, (b) density of dislocations and (c) lattice strain as a function of activation time

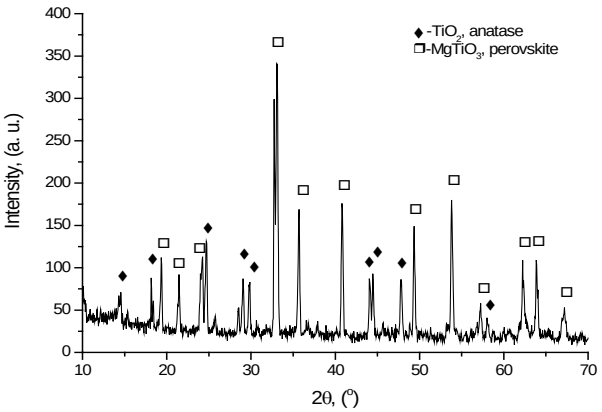


*Figure 2 :* XRD pattern of sample activated 120 min and sintered 3 h at 1100°C

Dilatometric analysis, given on figure 1, confirms the results obtained by X ray difractometry and thermal analysis [9]. 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 $Mg_2TiO_4$ [11].

Increased milling time to 120 minutes, as confirmed by SEM micrographs, Figure 3, lead to linking of most particles into solid agglomerates characterized by closed porosity that slows down the shrinkage process so the sintering process temperature increases and also the sintering time. This analysis also indicates the time required for non-isothermal sintering. Microstructural analysis has shown that mechanical activation not only increases the sintered sample density but also leads to increased neck contacts and strengthening of boundary grain zones. As a result of this, microstructures show that sample surface fractures have occurred between and over grains. According to the performed analysis the most homogenous microstructure was obtained for the sample activated for 120 minutes.

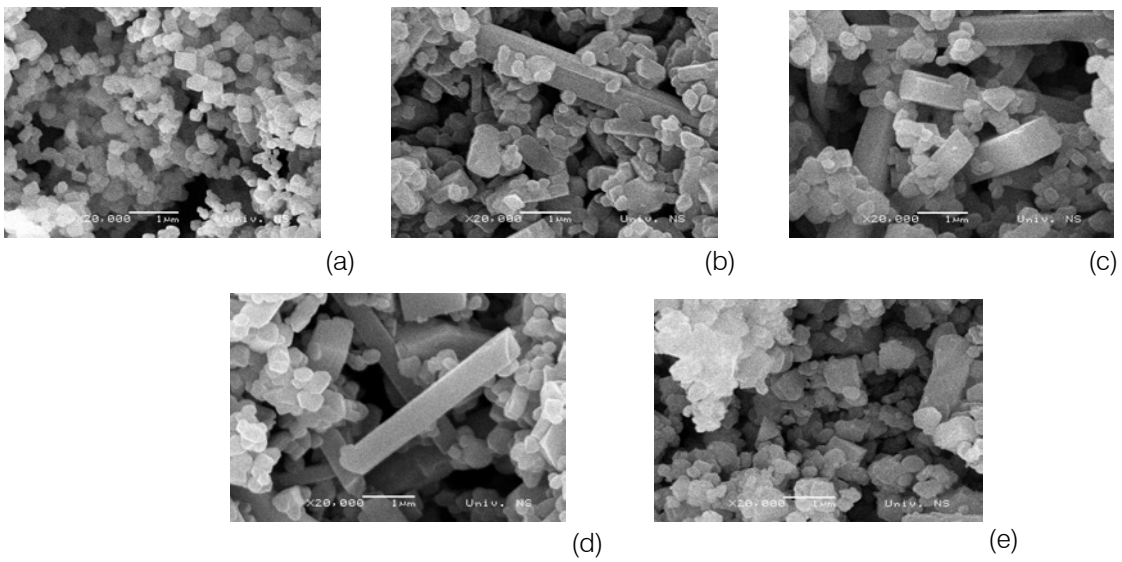


*Figure 3 :* SEM micrographs of samples activated (a)0,(b)15,(c)30,(d)60 and (e)120 min and sintered at 1100°C for 3 h

The most significant electric properties on which application of a dielectric material directly depends is the quality factor Q or the dielectric loss tangent angle $tg\delta$ and relative dielectric constant $\varepsilon_r$ [11].

Variation of synthesis parameters can give a material with defined properties. Concretely, using the example of the relative dielectric constant, it is noticeable that variation of the sintering time for the same duration of mechanical activation can select a certain $\varepsilon_r$ value.

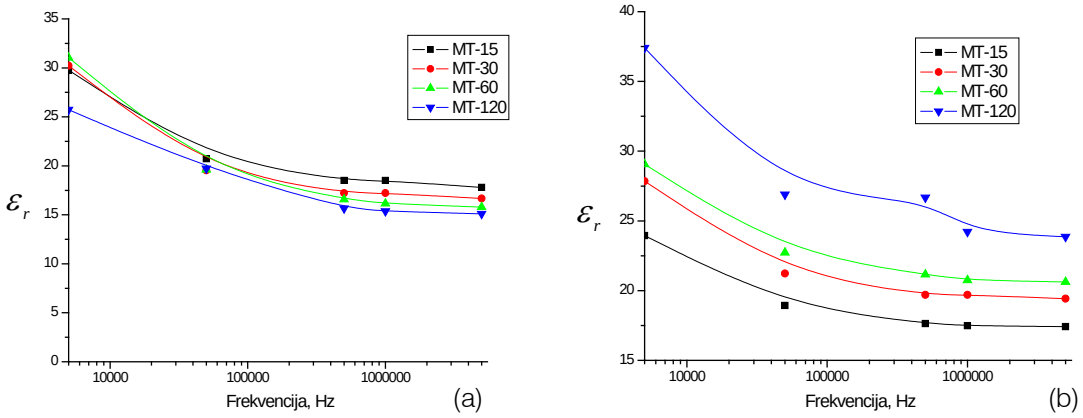


*Figure 4 :* $\varepsilon_r$ as a function of frequency for samples sintered 30 minutes (a) and 60 minutes (b) at 1100°C

Measurement results show that changes in the sintering time change the polarization of constant electric dipoles in $MgTiO_3$ that has a direct influence on the value of the relative dielectric constant. The lowest $\varepsilon_r$ value was obtained for the MT-120 sample sintered for 30 minutes, while a similar value was obtained for the MT-60 sample also sintered for 30 minutes. These results indicate if a material with a high $\varepsilon_r$ value is desired, one should set the synthesis parameters to mechanical activation of 120 and sintering time of 60 minutes. With the increase of frequency, $\varepsilon_r$ value decreses. Depending on requirements, variation of synthesis parameters can give predicted values for the relative dielectric constant.

The results obtained show that the quality factor increases with the increase in sintering time for activated samples. The quality factor also increases for increasing times of mechanical activation as a function of frequency. The results obtained for the quality factor show that synthesis parameters have a significant influence on electric properties of the sintered $MgTiO_3$ system. Increasing of the sintering time in combination with increasing the time of mechanical activation gives a material with a higher quality factor. With the increase of frequency, Q value increses, as well.

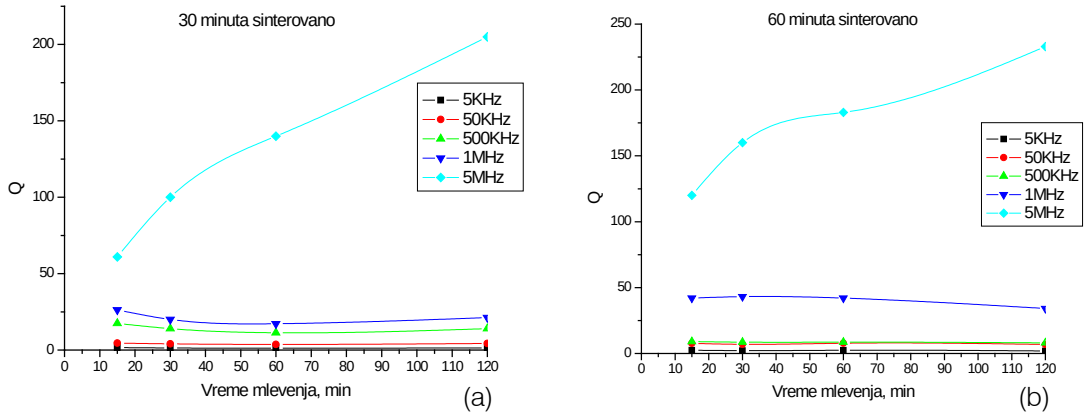


*Figure 5 :* Quality factor of frequency for samples sintered 30 minutes (a) and 60 minutes (b) at 1100oC

## III. Conclusions

Obtaining materials with advance defined properties is the main task of new materials science. The research subject of this paper were a stady of the influence of synthesis parameters of magnesium titanate ($MgTiO_3$).

Increasing the activation time leads to lowering temperature of the reaction compared with non-

activated samples. Basic changes in the material during mechanical activation occur on physical-chemical surface parameters thus changing the materials reactivity. Reduction of the povder particle size increases its specific surface and thus its reaction capability. Grinding $MgCO_3$ and $TiO_2$ powders increases their reactivity and accelerates solid state reactions. All analyses show that increasing the grinding time reduces the phase formation temperature and thus shortens the sintering duration.

One of the parameters set before new materials syntheses is the time needed to obtain them and accordingly the invested energy. Optimal duration of mechanical activation leads to reduced energy consumption, and thus reduction of the sintering temperature and time. The results obtained show that the worst properties are obtained for samples that were not mechanically activated. Increasing the sintering time in combination with increasing the time of mechanical activation gives a material with an increased quality factor. Depending on requirements, variation of synthesis parameters can give desired values for the relative dielectric constant.

Based on the results obtained in this work conditions have been created for controlling the structure of magnesium titanate through synthesis parameters thus enabling obtaining of materials with advance defined electric properties that can be widely applied in the field of electronics.

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