Science of Sintering, **41** (2009) 117-123

doi: 10.2298/SOS0902117F

UDK 622.785:661.846

Influence of Mechanical Activation on Structural and Electrical Properties of Sintered $MgTiO_3$ Ceramics

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Abstract:

The aim of this work was to analyze the influence of mechanical activation on the $MgCO_3$-TiO_2 system. Mixtures of $MgCO_3$-TiO_2 were mechanically activated for 15, 30, 60 and 120 minutes in a planetary ball mill and after that sintered at 1100^{0}C for 1h. XRD analyses were performed in order to give information about the phase composition and to determine a variety of microstructure parameters using Scherrer's method. Also, the effect of tribophysical activation and sintering process on microstructure was investigated by scanning electron microscopy. Electrical measurements were performed in order to determine electrical properties of sintered samples. Our conclusions are that the sample activated for 120 min showed the best electrical properties (ε_r=23.86, Q=233, ρ=0.38) and exhibited the best sinterability.

Keywords: *Sintering, $MgTiO_3$*

1. Introduction

Ceramic materials have been in use in many different areas of human wellbeing for a very long time. Materials based on magnesium titanates, $MgTiO_3$ and Mg_2TiO_4, are finding a variety of applications in microwave engineering. Materials applied in electronics are important fields of ceramic materials [1,2]. These materials differ extremely and have low dielectric loss in the microwave range and dielectric constant of 10-20 (Mg_2TiO_4 has a dielectric constant ε=14, while $MgTiO_3$ has ε=16).

Three stable phases of magnesium titanates ($MgTiO_3$, Mg_2TiO_4 and $MgTi_2O_5$) have been reported in literature [3]. It has been established that $MgTiO_3$ possesses an ilmenite structure, $MgTi_2O_5$ has a pseudobrookite structure and Mg_2TiO_4 has an inverse spinel structure [4]. Magnesium titanates melt at the temperatures from the interval 1732-1835 ^{0}C [5].

$MgCO_3$-TiO_2 ceramics are well known materials for temperature compensating capacitors and dielectric resonators, and require sintering temperatures over 1300^{0}C [6].

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Based on literature data it is well known that mechanical activation is a widely used method, which enhances the mixture homogeneity of the starting components; their reactivity, remarkably lowers the reaction temperature and hence, significantly reduces sintering temperature [7].

In this study, the authors have attempted to reduce the sintering temperature of the $MgCO_3$-TiO_2 system using a common part of the powder preparation route, the method of mechanical activation. The measured dielectric properties were discussed from the results based upon the densification, X-ray diffraction patterns along with the microstructures of sintered $MgTiO_3$ ceramics.

Experimental

As starting materials in this work, we used $MgCO_3$ (99.9% p.a.) and TiO_2 (99.9 p.a.) at a molar ratio 1:1. The powders were submitted to mechanical treatment in a planetary ball mill device (Fritsch Pulverisette 5), with zirconium oxide balls and vessels.
The ball to powder mixture mass ratio was 40:1. The milling process was performed in air for 15, 30, 60 and 120 minutes, and mixtures were denoted according to the applied time of activation as MT-00, MT-15, MT-30, MT-60 and MT-120.

Samples were heated in a tube furnace (Lenton Thermal Design Typ 1600) with a heating rate of 10^0C/min and when the temperature of the furnace reached 1100^0C, compacts were sintered isothermally in air atmosphere for 60 minutes. Sintered samples were denoted as MT_s-0, MT_s-15, MT_s-30, MT_s-60 and MT_s-120.

The morphology of obtained sintered pellets was characterized by scanning electron microscopy (JEOL JSM-6390 LV). The pellets were broken and covered by gold.

X-ray powder diffraction patterns after sintering were obtained using a Philips PW-1050 diffractometer with λCu-K_α radiation and a step/time scan mode of 0.05^o/sec.

The measurements of electrical properties were performed at a frequency of 5 MHz with a HIOKI 3532-50 HiTESTER device at a constant voltage mode. The "four-probe" configuration was used. The samples were prepared by painting silver electrodes on both sides following with thermal treatment at 120°C for 2h performed in order to improve the paint conductivity.

Results and discussion

In order to investigate the effect of mechanical activation on system's microstructure, scanning electron microscopy was performed. Scanning electron images, presented in Fig. 1, show a significant difference in powders sintered for 1h at 1100°C activated for 0-120 minutes. Evolution of microstructural constituents, grains and pores occurs during the sintering process, where along with sintering time increasing, adequate processes of grain growth and decreasing pore size take place. Fig. 1. (a) indicates that the non-activated sintered powder consists of two different kinds of grains: slightly connected polygonal spheres size of 0.7-1 μm and well sintered parts of 1.3-3 μm needles and polygonal discs of 6 μm in size, with great open porosity.

Densification process is observable within Fig. 1. (b) as well as the existence of several different kinds of grains, 300-400 nm small particles, 1.3-1.4 μm oval particles and polygonal particles in size of 3 μm. MT_s-30 and MT_s-60 micrographs showed porosity decrease along with polygonal grain growth from 3-5 μm in size.

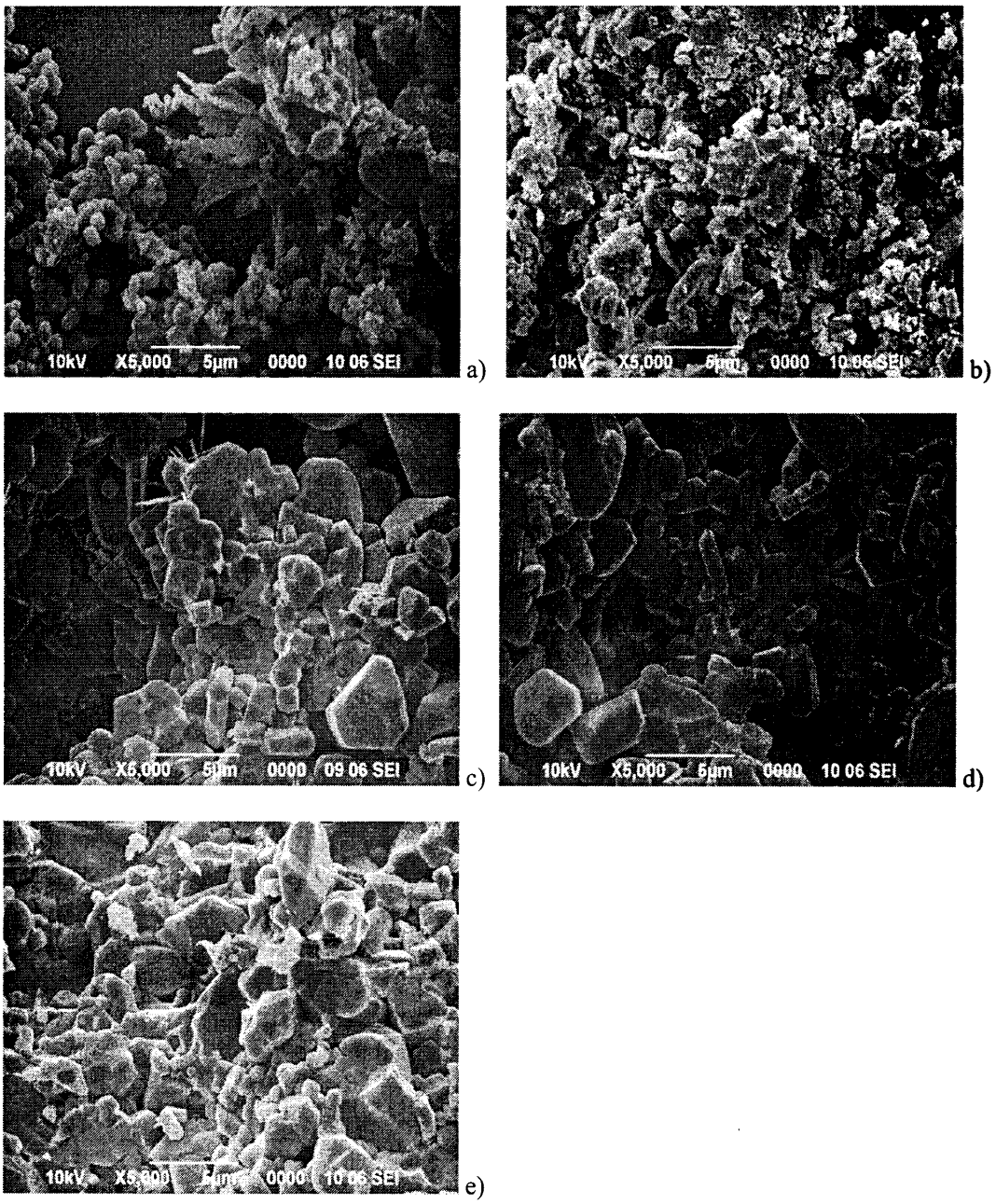

Fig. 1 Scanning electron micrographs of (a) MT_s-0, (b) MT_s-15, (c) MT_s-30, (d) MT_s-60 and (e) MT_s-120 powders sintered at 1100°C for 1h.

Finally, the MT_s-120 micrograph exhibits the best sinterability. The decrease in pore size is observed, which leads to intensive mass transportation process, strengthened grain boundaries and finally to better homogeneity.

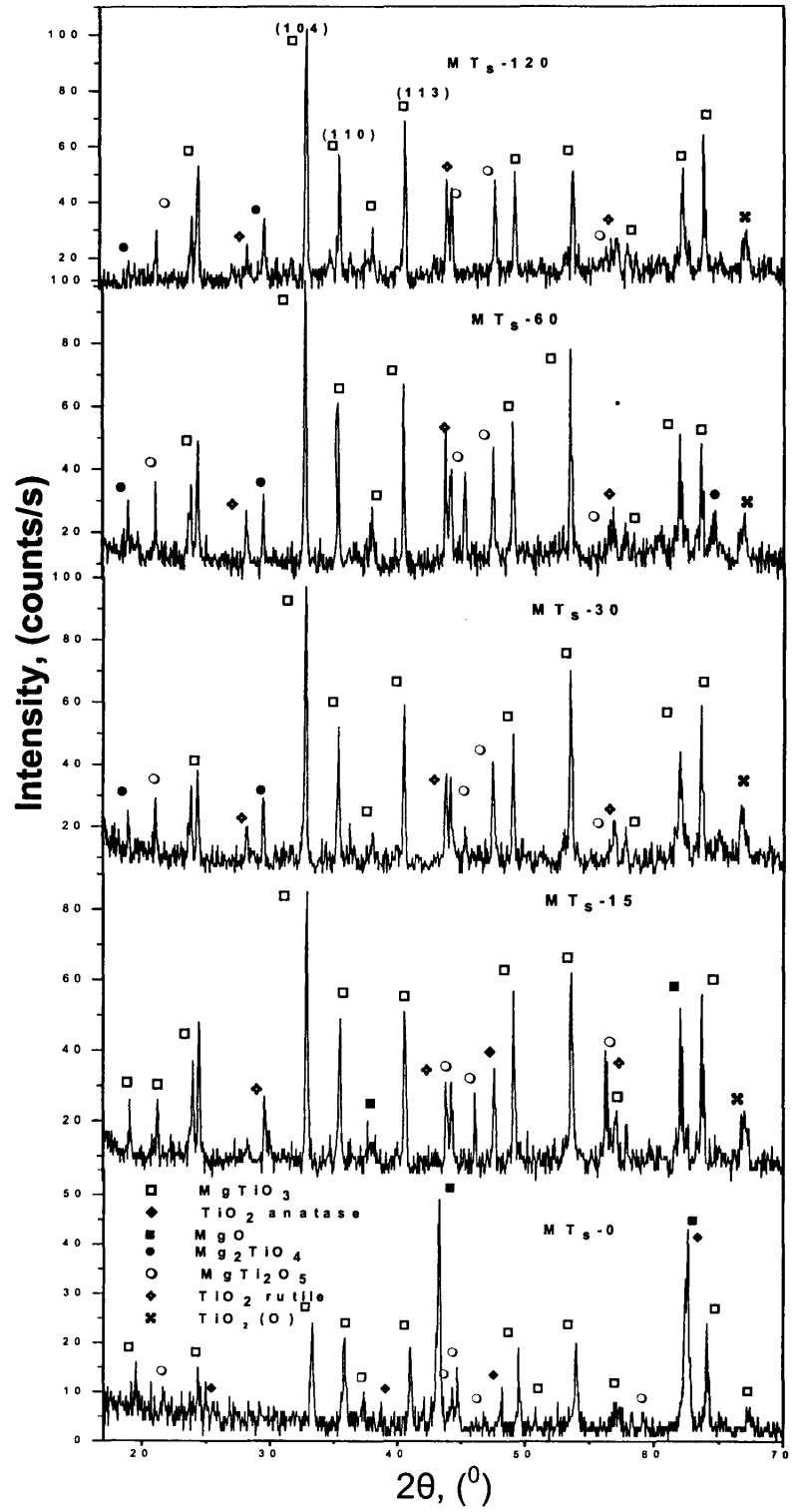

Fig. 2. X-ray diffraction patterns of MT_s-0, MT_s-15, MT_s-30, MT_s-60 and MT_s-120 powders sintered at 1100°C for 1h.

This is in accordance with the X-ray analysis. Fig. 2. shows the X-ray diffraction patterns of MT_s-0, MT_s-15, MT_s-30, MT_s-60 and MT_s-120 powders sintered at 1100°C for 1h. Identification of the obtained reflections was accomplished using JCPDS cards (79-0831 for $MgTiO_3$, 65-5714 for TiO_2 anatase, 77-0443 for TiO_2 rutile, 72-0021 for TiO_2 (o), 71-1176 for MgO, 76-2373 for $MgTi_2O_5$ and 79-0829 for Mg_2TiO_4). It is clearly visible that after heating we have the $MgTiO_3$ magnesium titanate phase with a small amount of MgO, metastable compound $MgTi_2O_5$ and TiO_2 anatase in a non-activated sample sintered at 1100°C for 1 h (XRDP of MT_s-0). That phase composition is in accordance with our previous investigations [8] and is the consequence of sintering the non-activated sample. The presence of the MgO phase was detected within sintered samples activated for 15 minutes, and for prolonged times of milling it's presence wasn't noticed. The very first appearance of the third, orthorhombic TiO_2 (o) modification, which represents the phase transition from anatase over TiO_2 (o) to the most stable form rutile is observed. Several literature data explained the phase transition from anatase over TiO_2 (orthorhombic) to rutile modification during mechanical activation [9,10]. This explains the disappearance of the anatase phase within diffraction patterns of samples activated 15-120 minutes and sintered at 1100°C for 1h. Diffraction patterns of activated and sintered samples MT_s-30 - MT_s-120 consist of the dominant $MgTiO_3$ phase and a mixture of small amounts of Mg_2TiO_4, $MgTi_2O_5$, TiO_2 rutile and TiO_2 (o) phases.

Recovery of the activated material, the disappearance of defects and grain growth are processes that occur during sintering. Also, it is obvious that the reflections of sintered samples are sharp and intensive, due to recrystallization.

Microstructure parameters were revealed from an approximation method using the well known Scherrer's equation [11] of sintered samples activated from 0-120 minutes: average particle size (D_{hkl}), density of dislocations (ρ_D) and lattice strain (e_{hkl}) are given in Tab. I for $MgTiO_3$ phase.

Tab. I Microstructure parameters revealed from approximation method for sintered samples for $MgTiO_3$ phase [11]

Phase	*(hkl)*	D_{hkl}, *(nm)*	$\rho_D \cdot 10^{10}$, *(cm^{-2})*	e_{hkl}
MT_s-0	(104)	45.26	14.65	0.267
	(110)	47.00	13.58	0.242
	(113)	43.58	15.69	0.227
MT_s-15	(104)	49.89	12.05	0.246
	(110)	47.00	13.58	0.242
	(113)	47.72	13.17	0.210
MT_s-30	(104)	51.65	11.25	0.239
	(110)	50.22	11.89	0.228
	(113)	47.72	13.17	0.210
MT_s-60	(104)	68.87	6.32	0.179
	(110)	58.25	8.84	0.197
	(113)	61.63	7.89	0.163
MT_s-120	(104)	79.53	4.74	0.154
	(110)	64.19	7.28	0.177
	(113)	67.28	6.63	0.148

The results of X-ray analyses and microstructure development are in accordance with dielectric properties of the sintered samples. The values of densities obtained before (d_o) and after sintering (d_s, given in gcm^{-3}), quality factor (Q, a reciprocal value of dielectric loss), dielectric loss ($tg\delta$), dielectric permittivity (ε_r) and specific resistance (ρ, given in MΩm) are given in Tab. II.

Tab. II. Electrical properties (at 5 MHz frequency), starting and sintered densities of samples activated 0, 15, 30, 60 and 120 minutes and sintered at 1100°C for 1h.

Sample	d_o (gcm^{-3})	d_s (gcm^{-3})	ε_r	Q	$tg\delta$ ($\cdot 10^{-3}$)	ρ ($M\Omega m$)
MT_s-0	1.95	2.30	15.16	150	6.7	0.15
MT_s-15	2.05	2.57	17.41	180	5.5	0.19
MT_s-30	2.27	3.01	19.43	160	6.2	0.35
MT_s-60	2.32	3.22	20.62	153	6.5	0.41
MT_s-120	2.53	3.49	23.86	233	4.3	0.38

The electrical measurements pointed out that dielectric permittivity of the specimens increased with activation time reaching its highest value for the sample activated 120 minutes. Also, densification is the greatest within the sample activated 120 minutes. It is believed that density plays an important role in controlling dielectric loss, as has been often found in other microwave dielectric materials [12]. The Q value is generally affected not only by the lattice vibrational modes, but also by pores, secondary phases, impurities, lattice defects, crystallizabillity and inner stress [13]. According to our analyses, since a higher density resulted in a higher dielectric permittivity owing to a lower porosity for the fixed sintering temperature and since the amount of the secondary phase is not negligible, as observed from XRD patterns, the effect of the poly-phase mixture on dielectric permittivity change is equal as the density effect. The increase in activation time is beneficial to the phase structure and densification after sintering and crystallizability until the Q value reaches its highest value in all the observed samples.

This suggests that, for the activation and sintering conditions we used, a higher density, phase composition and the homogeneity of morphology are dominantly responsible for the higher values of dielectric permittivity of the samples.

Conclusions

The phase composition in $MgCO_3$-TiO_2 solid solutions along with the microstructures and electrical properties were studied. The main conclusions are:

- With the increase in activation time, the evolution of microstructural constituents, grain growth, decrease of pore size along with densification are observed within SEM micrographs during the sintering process.
- The XRD patterns of sintered samples showed the existence of $MgTiO_3$ magnesium titanates as the dominant phase with a certain amount of Mg_2TiO_4, $MgTi_2O_5$, TiO_2 rutile and TiO_2 (o) phases.
- Also, microstructural parameters revealed from an approximation method confirmed the processes of particle size growth along with the decrease in crystal lattice defects.
- The electrical properties are a consequence of the crystal structure caused by the milling process of starting powders. 120 minutes of activation and the ratio of MgTiO3 and the rest of phases are responsible for the best electrical properties of all samples obtained after sintering (the highest Q factor of 233, relative dielectric constant ε_r of 23.86 and low dielectric loss $tg\delta$ of 0.0043).

Acknowledgements

This study was supported by the Ministry of Science and Technology of the Republic of Serbia (Project 142011G) and Project F/7 supported by the Serbian Academy of Sciences and Arts.

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Садржај: *Циљ овог рада био је анализа утицаја механичке активације на систем $MgCO_3$-TiO_2. Смеше $MgCO_3$-TiO_2 су механички активиране у планетарном млину са куглама у трајању од 15, 30, 60 и 120 минута и након тога синтероване на 1100^{0}C 1h. Ради утврђивања фазног састава и промена микроструктурних параметара, Шереровом методом, урађена је рендгено-дифракциона анализа. Ефекти механичке активације и процеса синтеровања на микроструктуру испитивани су скенирајућом електронском микроскопијом. У циљу одређивања електричних својстава синтероаних узорака извршена су електрична мерења. Закључак нашег рада је да узорак синтерован 120 минута показује најбоља електрична својства (ε_r=23,86; Q=233; ρ=0,38) и испољава најбољу синтерабилност.*

Кључне речи: *синтеровање, $MgTiO_3$*