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INFLUENCE OF SYNTHESIS PARAMETERS ON ELECTRICAL PROPERTIES OF SISTEMS $MgO\text{-}TiO_2$

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Abstract: In this paper magnesium carbonate ($MgCO_3$) and titanium-dioxide (TiO_2), crystalline modification rutile were used as starting powders.. Process of sintering can be enhanced if mechanical activation precedes. Mechanical activation of the starting mixture was performed by high energy ball milling using ZrO balls and vessels with ball to powder mass ratio 40:1. The observed grinding times were 15, 30, 60 and 120 minutes. The isothermal sintering of compacted powders was conducted at 1100°C during 30, 60 and 180 minutes. For specimens synthesized in such a manner, microwave dielectric properties were measured, quality factor *Q,* specific electrical resistivity (ρ) and the dielectric constant ($\boldsymbol{\varepsilon_r}$).

Keywords: magnesium carbonate, titanium-dioxide, dielectric properties.

INTRODUCTION

Development of microwave dielectric resonators and antennas for applications in communication systems such as cellular phone, direct broadcasting satellite (DBS) and global positioning systems has been rapidly progressing in the past decade [1, 2]. Recently, microwave dielectrics are widely used as resonators, filters and oscillators [3]. The dielectric characteristics required for microwave resonator are high dielectric constant (ε_r) to reduce the size of resonators and high quality factor (Q) for achieving prominent frequency selectivity and stability [1]. Moreover, low-sintering temperature is also required to match with low-loss and low-melting point conductors in fabrication of dielectric devices [4]. 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. $MgCO_3\text{-}TiO_2$ (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 1300°C.

In this study, to reduce the sintering temperature of $MgCO_3\text{-}TiO_2$ system, the method of mechanical activation, a common part of the powder preparation route, was chosen. The measured dielectric properties were discussed from the results based upon the densification, X-ray diffraction patterns and the microstructures of ceramics. The authors have attempted to reveal the influence of milling conditions on structural and dielectrical properties of sintered magnesium-titanate ceramics.

1. 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 weighed out. The powders were submitted to mechanochemical treatment, in a planetary ball mill 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.

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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 placed 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 for precise measurements of specimen's diameter, thickness and mass.

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_α radiation and a step scan mode of 0.02°/2 s. The morphology of obtained powders was characterized using scanning electron microscopy (JSM-6460 LV JEOL).

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 followed with thermal treatment at 120°C for 2 h performed in order to improve the paint conductivity.

2. RESULTS AND DISCUSSION

According to our X-ray analysis [5], 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 after 30 min of mechanical treatment. Microstructure parameters revealed from an approximation method [6] of ball-milled $MgCO_3$-TiO_2 powder mixture: particle size (D_{hkl}), density of dislocations (ρ_D) and lattice strain (e_{hkl}) are presented in Fig. 1. After sintering, a magnesium-titanate ($MgTiO_3$) phase along with small amounts of unreacted TiO_2 [7] phase is observed (Fig. 2). Also, phase identification has been done using JCPDS cards 01-079-0831 and 01-074-1940 for magnesium-titanate and titan-dioxide, respectively.

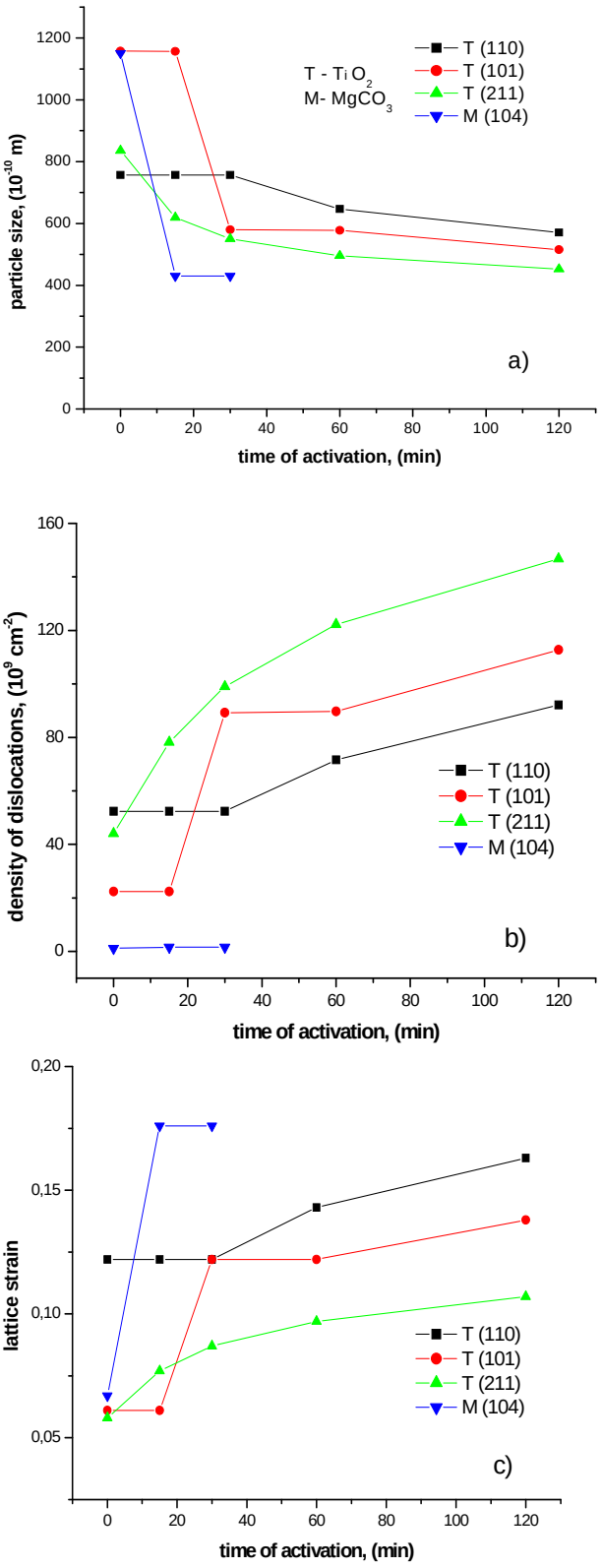

Figure 1. Microstructure parameters: (a) particle size, (b) density of dislocations 120 min and sintered 3 h at 1100°C and (c) lattice strain as a function of activation time.

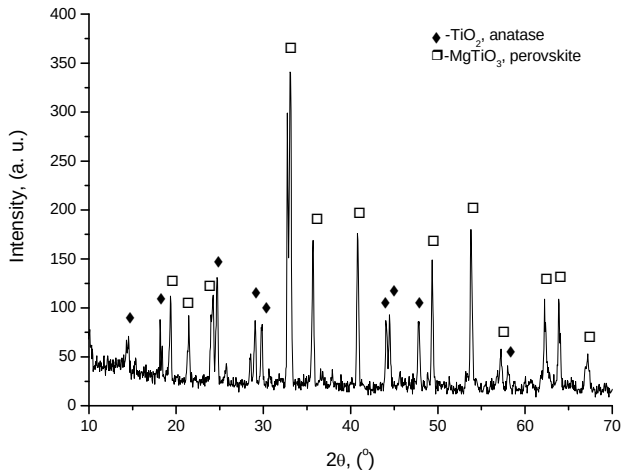

Figure 2. XRD pattern of sample activated

Mechanical activation is characterized by crystallite size reduction and increase in dislocation density and lattice strain, and our experiment confirmed these facts. Mechanical activation leads to the reduction in cohesive dispersion domains for all directions observed, the number of defects within the material rises and that reclaims the diffusion of MgO and TiO_2 atoms, which leads to a solid-state reaction. The evolution of microstructure constituents, grains and pores occur during the sintering process, where with the increase of temperature and prolonged time of sintering, the adequate processes of grain growth and decrease of pore size are taking place. The results of microstructure development are in accordance with dielectric properties of the samples. The values of density obtained before and after sintering (d_0 and d_s, given in gcm^{-3}), quality factor (Q), relative dielectric permittivity (ε_r) and specific resistance (ρ, given in Ωm) are given in Table 1. The electrical measurements pointed out that dielectric permittivity of the specimens increased with activation time reaching its maximum for the sample activated during 120 min. It is believed that the densities play an important role in controlling dielectric loss, as has been often found in other microwave dielectric materials [8].

The Q value is generally affected not only by the lattice vibration modes, but also by the pores, the second phase, the impurities, the lattice defect, crystallizability and inner stress [9, 10]. According to our analysis, a higher density resulted in higher dielectric permittivity owing to the lower porosity for the fixed sintering temperature. The increase in activation time is beneficial to the densification after sintering and crystallizability until the Q value reaches the maximum. A further increase in activation time will probably result in the appearance of abnormal grains and pores after sintering process and consequently lead to the reduction of the Q value. This suggests that, for the activation and sintering conditions that we used, a higher density and the homogeneity of morphology are dominantly responsible for the higher values of dielectric properties of the samples.

Table 1. Dielectric properties (at 5 MHz frequency) and densities of samples non-activated and activated 15, 30, 60 and 120 min and sintered at 1100°C for 3 hours.

Sample	d_0 (gcm^{-3})	d_s (gcm^{-3})	ε_r	**Q**	$tg\delta$	ρ (Ωm)
MT-00	1.95	2.39	16.25	73	0.015	0.68
MT-15	2.05	2.69	17.25	82	0.012	0.55
MT-30	2.27	3.13	16.90	175	0.005	0.41
MT-60	2.32	3.32	18.01	242	0.004	0.22
MT-120	2.53	3.72	19.22	280	0.003	0.21

3. CONCLUSIONS

In this article the influence of mechanical activation of the $MgCO_3$-TiO_2 system on structural and dielectric properties of sintered magnesium-titanate ceramics has been examined. It was found that the first significant appearance of $MgTiO_3$ phase along with all the starting phases was established after 30 min of mechanical activation. A magnesium-titanate, $MgTiO_3$, phase with small amount of TiO_2 in all samples has been synthesized successfully after the sintering process. Also, the process of mechanical activation leads not only to the decrease in crystallite size and increase in dislocation density and lattice strain, but to the significant reduction in sintering temperature too. Moreover, the MT-120, sample activated 120 min and sintered at 1100°C for 3 hours exhibited the best microwave dielectric properties: ε_r of 19.22, Q value of 280 (at 5 MHz), and the lowest dielectric loss of 0.003.

REFERENCES

[1] W. Werising, in: B. C. H. Sreele (Ed.), *Electronic Ceramics*, Elsevier, London (1991) 67.

[2] G. Wolfram, H. E. Gobel, *Existence range, structural and dielectric properties of $Zr_xTi_ySn_zO_4$ ceramics (x+y+z=2),* Materials Research Bulletin 16 (1981) 1455−1463.

[3] S. Nishigaki, *FC Rep.* 5 (1987) 413, Trans: FC Ann. Rep. Oversea Reader (1988) 32.

[4] W. W. Cho, K. Kakimoto, H. Ohsato, *Microwave dielectric properties and low-temperature sintering of $MgTiO_3$-$SrTiO_3$ ceramics with B_2O_3 or*

CuO, Materials Science Engineering B, 121 **(**2005) 48−53.

[5] V. Petrović, *Sintering kinetics of MgO-TiO_2 system*, Science of Sintering 38 (2006) 287−292.

[6] Lj. Karanović, *Primenjena kristalografija* [Applied Crystallography], Univerzitet u Beogradu, Beograd, 1996 (in Serbian).

[7] N. Stubicar, A. Tonejc, M. Stubicar, *Microstructural evolution of some MgO-TiO_2 and MgO-Al_2O_3 powder mixtures during high-energy ball milling and post-annealing studied by X-ray diffraction*, Journal of Alloys and Compounds, 370 (2004) 296−301.

[8] J. Zhu, E. R. Kipkoech, W. Lu, *Effects of $LnAlO_3$ (Ln=La, Nd, Sm) additives on the properties of $Ba_{4.2}Nd_{9.2}Ti_{18}O_{54}$ ceramics,* Journal of the European Ceramic Society 26 (2006) 2027−2030.

[9] C.-L. Huang, *Liquid phase sintering of $MgTiO_3$-$CaTiO_3$ microwave dielectric ceramics*,Materials Chemistry and Physics 78 (2002) 111−115.

[10] L. W. Lei, Z. Y. Fu, J. Y. Zhang, *Influence of sintering temperature on microstructure and magnetotransport properties of $La_{0.8}Na_{0.2}MnO_3$ ceramics*, Materials Letters 60 (2007) 970−973.

УТИЦАЈ ПАРАМЕТАРА СИНТЕЗЕ НА ЕЛЕКТРИЧНА СВОЈСТВА СИСТЕМА MgO-TiO_2

Сажетак: У овом раду као полазни прахови коришћени су магнезијум-карбонат ($MgCO_3$) и титан-диоксид (TiO_2), кристална модификација рутил. Еквимолска смеша полазних прахова механички је активирана млевењем у високоенергетском планетарном млину са ZrO куглама и масеним односом кугли и праха 40 : 1. Време млевења полазне смеше је 15, 30, 60 и 120 минута. Изотермско синтеровање испресованих узорака извршено је на температури од 1100 °C у трајању од 30, 60 и 180 минута. За синтероване узорке проучавана су диелектрична својства: фактор доброте (Q), специфична електрична отпорност (ρ) и релативна диелектрична константа (ε_p).

Кључне речи: магнезијум-карбонат, титан-диоксид, диелектрична својства.