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Investigation of Sintering Kinetics of Magnesium Titanate

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Abstract:

Obtaining new materials including sintered electronic materials using different procedures is the consequence of long complex and expensive experimental work. However, the dynamics of expansive development of electronic devices requires fast development of new materials, especially sintered oxide materials. The recent rapid development of electronics is among other things due to development and improvement of new components based on titanate ceramics. Research in this work has included an experimental study of the synthesis of dielectric ceramics in the system $MgCO_3 – TiO_2$. Starting powders were mechanically activated by milling in a high energy planetary mill for different times. Samples were prepared for isothermal sintering at 1100^oC by dual pressing of powders into cylindrical samples in a hydraulic press.

Keywords: *Sintering kinetics, $MgTiO_3$, Dielectric ceramics.*

1. Introduction

In advanced technologies, powder preparation for the synthesis of new materials is performed by mechanical activation – intensive transfer of mechanical energy to the powders, in specially constructed mills. Mechanical activation leads to controlled disorganization and destruction of a material [1]. As the reaction ability of a material is the consequence of its structure, the disorganization and destruction processes occurring during mechanical activation of powders, further influence synthesis and sintering of materials using activated powder.

Sintering is a method used most often for obtaining polycrystal materials. It is a set of complex and linked processes occurring among particles and inside particles of a disperse system during consolidation [2]. During sintering of polydisperse powders, shrinkage occurs, density increases and porosity of a disperse material decreases and at the same time partial recovery of the crystal lattice occurs. Sintering starts by formation of a contact surface between powder particles, followed by pore filling with material due to mobility of the construction elements of the crystal lattice at high temperatures. The essence of these processes is that the electronic system approaches an equilibrium state, whose ideally periodic

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space contains a defect structure [3].

Magnesium titanate ($MgTiO_3$) is obtained by the sintering procedure from starting powders in the system $MgCO_3 – TiO_2$, and it is a member of rutile ferroelectric ceramics. Due to good electric properties $MgTiO_3$ has been lately widely applied in the construction of microwave frequency resonators and antenna in filters and oscillators to be applied in communication systems, such as mobile phones, satellite systems and GPS (global positioning system) devices [4]. It is also applied in the construction of integrated circuits and actuators. Magnesium titanate also represents a base material in the construction of multilayered condensers. Sintered polycrystal magnesium titanate is applied in electronics due to its properties linked to its crystal structure, i.e. dielectric polarization [5].

2. Experimental

Magnesium carbonate ($MgCO_3$) and titanium dioxide (TiO_2) starting powders, were measured to make a mixture with the molar ratio $MgCO_3 : TiO_2 = 1 : 1$ [1]. An equimolar mixture of starting powders was mechanically activated by milling in a high energy planetary mill with zirconium oxide balls (Fritsch Pulverisette 5) and ball:powder ratio of 40:1. Depending on the milling time, five mixtures were analyzed in this work (non-activated mixture and four mixtures activated for different times – 15 minutes, 30 minutes, 60 minutes and 120 minutes), designated as MT-00, MT-15, MT-30, MT-60 and MT-120 respectively. Sample preparation for sintering was performed by dual pressing of powders into cylindrical samples in a hydraulic press. After preparation of samples with certain dimensions, mass and thus starting density ρ_o, isothermal sintering was performed at the temperature of 1100 °C for different times (30, 60 and 180 minutes). In aid of obtaining magnesium titanate with properties defined in advance a comprehensive analysis [5, 6] from many different aspects was performed in view of determining synthesis parameters. In this work the part related to the sintering kinetics is presented.

3. Results and discussion

3.1. Sintering kinetics determined by phenomenological analysis

After mechanical activation samples were pressed with a pressing pressure of 400 MPa. After pressing all samples (non-activated and activated for 15, 30, 60 and 120 minutes) their starting density ρ_0 was determined based on measuring the mass and geometric parameters of the green samples, $(\rho = m/V = 4m/h\pi D^2)$. All green samples were sintered non-isothermally until the isothermal sintering temperature was reached. They were sintered at this temperature for different times of 0, 30, 60 and 180 minutes.

Analysis of the volume change of samples before and after sintering ($\Delta V/V_0$), enabled following of the sintering kinetics. As $V=m/\rho$, (where m – mass, ρ – density, and V – sample volume) the $\Delta V/V_0$ ratio can be presented as:

$$\frac{\Delta V}{V_0} = \frac{V_0 - V_s}{V_0} = \frac{\frac{m}{\rho_0} - \frac{m}{\rho_s}}{\frac{m}{\rho_0}} = \frac{\frac{\rho_s - \rho_0}{\rho_0 \rho_s}}{\frac{1}{\rho_0}} = \frac{\rho_s - \rho_0}{\rho_s} \qquad (1)$$

Fig. 1 shows relative change of sample density for all five investigated mixtures sintered at 1100 °C. As the fig. clearly shows, the sintering density is influenced by the sintering time and also the duration of mechanical activation.

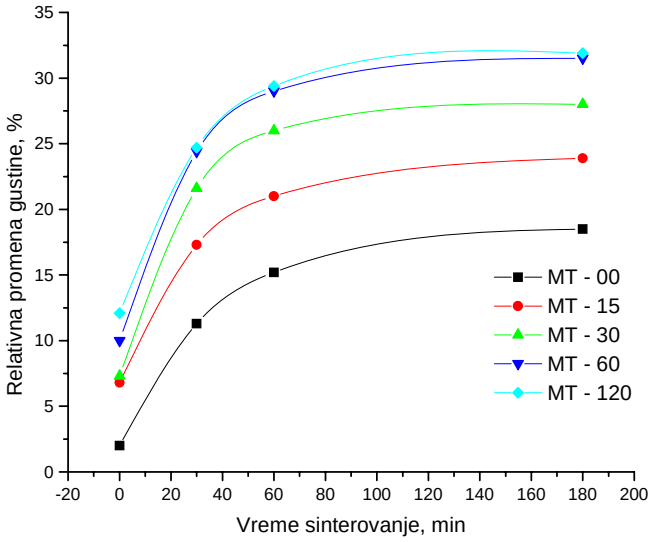

Fig. 1. Relative change of density as a function of sintering time for analyzed mixtures sintered at 1100 °C.

Extension of the sintering time leads to an increase in the density of sintered samples. The influence of sintering time is visible for all samples – non-activated and activated for different times. The conclusion can be reached that the duration of sintering has the smallest influence on the non-activated sample, confirming theoretical assumptions and validating introduction of mechanical activation prior to the sintering process. If the question is the influence of the duration of mechanical activation on sample density, it can be clearly noted that increase in the duration of mechanical activation increases relative changes in the density of sintered samples.

Tab. I shows functional dependencies of the relative change of sample density, where coefficient A represents a parameter defining the influence of the sintering process and it increases with the time of mechanical activation. Coefficient B represents a parameter defining the degree of densification and it also increases with the increase in activation time.

Tab. I. Relative change of density as a function of the sintering time.

Sample designation	Relative change of density (ρ_R)	Coefficients
MT - 00	$\rho_R = A - \frac{19}{1 + B \cdot t}$	A = 20,6 B = 0,04
MT – 15	$\rho_R = A - \frac{19}{1 + B \cdot t}$	A = 25,5 B = 0,05
MT – 30	$\rho_R = A - \frac{19}{1 + B \cdot t}$	A = 29 B = 0,06
MT – 60	$\rho_R = A - \frac{23}{1 + B \cdot t}$	A = 33 B = 0,07
MT – 120	$\rho_R = A - \frac{23.5}{1 + B \cdot t}$	A = 33,5 B = 0,075

Sample MT – 120 after three hours of sintering at the temperature of 1100 °C has the highest density of 3.72 g/cm^3. This attained density of a sintered sample represents 93% of the theoretical density.

3.2. Sintering Kinetics According to Gropyanov

Gropyanov (V. Gropyanov) and many other authors assumed that sintering of crystal powders with no liquid phase occurs by volume diffusion of vacancies. In his work [8] he showed that kinetics of the sintering process can be generally determined with two parameters, the boundary densification degree () and sintering rate constant (*K*). According to Gropyanov, the sintering kinetics can be described by the following equation:

$$C = C_{\infty} \frac{K \cdot t}{1 + K \cdot t} \tag{2}$$

where: (*C* – the densification degree; – the boundary densification degree; *K* – the sintering rate constant; *t* – the sintering time (time the densification degree is reached)).

Equation (2) can be represented as a reciprocal value:

$$\frac{1}{C} = \frac{1}{C_{\infty}} + \frac{1}{C_{\infty} \cdot K} \cdot \frac{1}{t} \tag{3}$$

that is a straight line $y=a+bx$, where: $y=1/C$; $x=1/t$; $a=1/$ and $b=1/$.

When investigating isothermal sintering, kinetics according to Gropyanov can be followed through dimensional changes, i.e. through the densification degree defined with parameter *C*:

$$C = \frac{\rho_s - \rho_0}{\rho_t - \rho_0} \tag{4}$$

where: (ρ_s – the density after sintering; ρ_0 – the starting sample density; ρ_t – the theoretical density).

According to Gropyanov, the sintering kinetics can be described by equation (3), but the sintering kinetics can be followed by equation (4), so equation (5) was formed:

$$\frac{1}{C} = \frac{1}{C_{\infty}} + \frac{1}{C_{\infty} \cdot K} \cdot \frac{1}{t} = \frac{\rho_t - \rho_0}{\rho_S - \rho_0} \tag{5}$$

Equation (5) represents a straight line $y = A + B \cdot x$,
where: $y = 1/C$; $x = 1/t$; $A = 1/C_{\infty}$ and $B = 1/C_{\infty} \cdot K$.

A formal mathematical analysis showed that curves characterized by the dependence *1/C* as a function of *1/t* (fig. 2) can be described with general equations of the first order for all samples (MT-0, MT-15, MT-30, MT-60 and MT-120).

The dependence *1/C* as a function of the sintering time and activation time for the sintering temperature of 1100 °C is given in Tab. II.

Tab. II. Dependence *1/C* for the sintering temperature of 1100 °C

Sintering time t[min]	Activation time				
	0 min	15 min	30 min	60 min	120 min
	1/C				
0	41,0	13,0	9,60	6,46	4,2
30	8,20	4,50	2,66	2,24	1,77
60	5,85	3,75	2,33	1,86	1,59
180	4,65	3,09	2,01	1,68	1,20

Based on equation (5) and the results presented in table 2 fig. 2 is obtained that graphically illustrates the dependence of the reciprocal value of the densification degree or Lenel's parameter (*1/C*) on the reciprocal value of the sintering time (*1/t*).

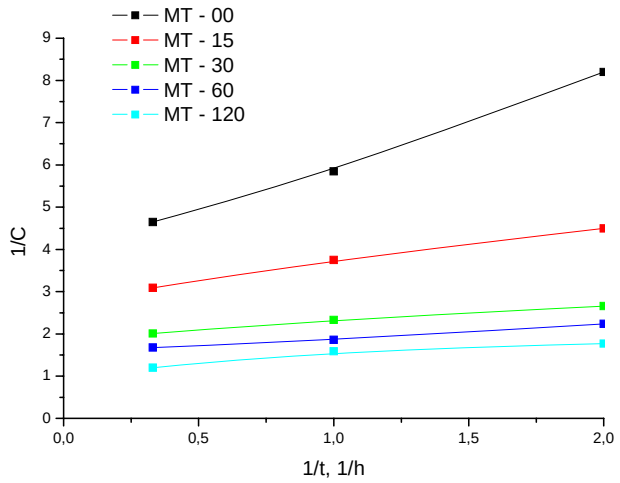

Fig. 2. Dependence of *1/C* on *1/t* for the sintering temperature of 1100 °C.

For all analyzed samples the presented dependencies can be characterized as linear, i.e. the obtained graphics show a linear dependence of the reciprocal value of the densification degree or Lenel's parameter (*1/C*) on the reciprocal value of the sintering time (*1/t*), as shown by equations (2) and (5). This confirms that the theory of Gropyanov can be applied to the sintering kinetics of magnesium titanate. A further analysis can be made now to determine optimal synthesis parameters and in this case these parameters are the duration of mechanical activation and the sintering time. As shown by Tab. II, only these two parameters will be followed.

Determination of the linear coefficient enabled calculation of parameters C_∞ (boundary densification degree) and K (sintering rate constant), that are shown in fig. 3.

The boundary densification degree increases with the increase in activation time and this dependence can be followed in fig. 3, as can be the dependence of the sintering rate constant, that also increases until certain duration of mechanical activation.

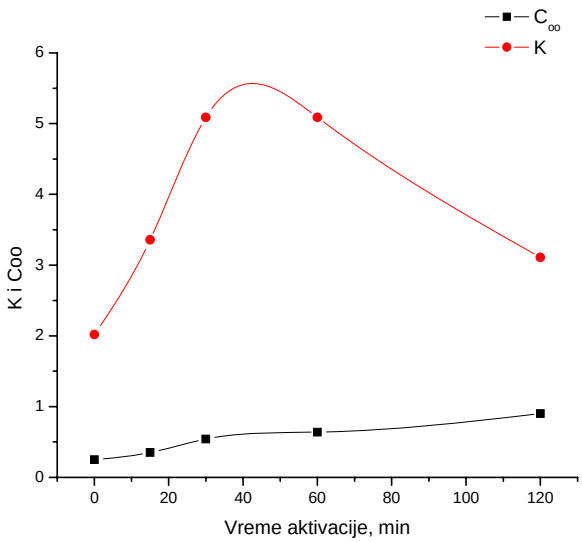

Fig. 3. Dependence of the boundary densification degree (C_∞) and sintering rate constant (K) on the activation time.

The boundary densification degree indicates that extending the activation time increases this parameter and this is in accordance with the results obtained from measuring the density of sintered samples. The density of sintered samples increases with the increase in the milling time. This justifies mechanical activation.

The boundary densification degree is characterized by a linear function described in equation 6:

$$C_{\infty} = 0.25 + 0.00416 \cdot t \quad (6)$$

With the increase in activation time, t, equation (6) described the behavior of the boundary densification degree.

The parameter characterizing the sintering rate constant increases until 60 minutes of milling, and after continuing milling this sintering rate constant starts to decrease. This is the first indicator that warns that the activation time cannot be limitless.

The sintering rate constant K, can be observed in two ranges. Up to 60 minutes of mechanical activation this constant increases linearly according to equation 7:

$K = 2 + 0{,}1 \cdot t$; in the interval 0 – 60 minutes (7)

This dependence shows an increase in the sintering rate constant with the increase of the duration of mechanical activation.

In the range over 60 minutes, the sintering rate constant decreases according to the dependence described with equation 8:

$K = 7{,}2 - 0{,}033 \cdot t$; for the range over 60 minutes (8)

The sintering rate constant after 60 minutes of grinding linearly decreases with the increase in sintering time.

One of the parameters set before synthesis of new materials is the time needed to obtain them and the corresponding invested energy. Optimal duration of mechanical activation will reduce energy consumption and thus decrease the sintering temperature and reduce the sintering time.

4. Conclusion

Sintering kinetics was followed by phenomenological analysis and the theory of Gropyanov. This work shows that the theory of Gropyanov can be applied to the sintering process of magnesium titanate. The boundary densification degree shows that its value increases with increase in the duration of mechanical activation and this is in accordance with the results obtained for measuring the density of sintered samples. The sintered sample density increases for increased milling times. This justifies mechanical activation. The sintering rate constant, grows until 60 minutes of milling, and after milling continues this sintering rate constant starts to decrease. This is one of the first indicators that the time of mechanical activation cannot be limitless. One of the parameters set before the synthesis of new materials is the time needed to obtain them and the corresponding energy needed. Optimal duration of mechanical activation leads to reduced energy consumption and thus to reduction of the sintering temperature and shortening of the sintering time. It can be concluded that the duration of the sintering process has the lowest influence on the non-activated sample, confirming theoretical assumptions and justifying introduction of mechanical activation of the system.

5. References

1. V. V. Petrovic, *Sinteza i svojstva dielektrične keramike sistema MgO-TiO_2* Doktorska disertacija, 2007.

2. S. M. Radić, *Naučno–tehnička terminologija*, Edicija nauka o materijalima 2,CMS i ITN SANU, 1984.
3. M. M. Ristić, *Principi nauke o materijalima*, Posebno izdanje knjiga DCXVII, SANU, Beograd, 1993.
4. I. M. Reaney, D. Iddles, *J. Am. Ceram. Soc.*,89, 2006, 2063-2072
5. V. Petrovic, *Sci. Sintering,* Vol. 38, No. 3, Sept. – Dec., 2006. 287-292.
6. Petrović V. V, Maričić A, Labus N, Ristić M. M. Sci. Sintering.Vol. 39. No.1. Jan.-Apr. 2007. 59-65.
7. Gropyanov V, Mogilensij V. Trudy Sesojuzmov institute ogmeuporov. 39. 1967. P.194.

Садржај: *Добијање нових материјала, па тако и синтерованих електронских материјала, различитим процесним поступцима, последица је дугог сложеног и скупог експерименталног рада. Међутим, динамика експанзивног развоја електронских уређаја захтева и брзи развој нових материјала, посебно синтерованих оксидних материјала. Нагли развој електронике у последњим годинама условљен је, између осталог, развојем и усавршавањем нових компонената и на бази титанатне керамике. Истраживања у овом раду су обухватила експериментална проучавања синтезе диелектричне керамике система $MgCO_3$ – TiO_2. Полазни прахови механички су активирани млевењем у високо енергетском планетарном млину у различитим временским периодима. Припрема узорака за изотермско синтеровање на 1100°C обављена је двостраним пресовањем прахова у цилиндричне узорке у хидрауличкој преси.*

Кључне речи: *Кинетика синтеровања, $MgTiO_3$, диелектрична керамика.*