# Advantages of Combined Sintering Compared to Conventional Sintering of Mechanically Activated Magnesium Titanate

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*Abstract:*

*In this article, the advantages of combined sintering in comparison with the conventional one, of mechanically activated magnesium titanate ceramic were investigated. The stoichiometric mixtures of MgO and TiO₂ were mechano-chemically activated for 0, 10, 40, 80 and 160 minutes by ball milling and then isostatically pressed (CIP) to form green bodies. Conventional sintering was realized by heating up to 1400 °C and hold for 30 minutes in air atmosphere. Resulting ceramic samples with closed porosity were post-sintered by pressure assisted technique Hot Isostatic Pressing (HIP) at 1280 °C/3h in argon atmosphere with a pressure of 200 MPa. The best results were observed in the case of samples post-sintered by HIP, when single-phase MgTiO₃ samples with relative density of 96% were prepared.*

Keywords: *Sintering, Ceramics, Magnesium titanate.*

## 1. Introduction

In the fabrication of ceramic components, important achievement is to reach full or almost full density of ceramics. In the last decades quite large number of sintering techniques besides conventional sintering method was developed. Consolidation of ceramic green bodies by these techniques (e.g. spark plasma sintering, microwave sintering, two step sintering) are preferably used for materials, which processing is difficult because of the unsuiTab. microstructure, final density or phase purity point of view.[1-5]

Magnesium titanate is a ceramic material widely used as resonators, filters and antennas for communication systems operating at microwave frequencies and capacitors.[6,7] In the literature, various methods for $MgTiO_3$ fabrication were presented, such as solid-state reactions, co-precipitation or sol–gel route.[6,8,9] Few secondary phases were often detected along with $MgTiO_3$ phase ($MgTi_2O_5$, $Mg_2TiO_4$).[10-12] Preparation of pure $MgTiO_3$ by solid state reaction was the aim of many papers. Magnesium titanate obtained by sintering process without additives reached density values less than 95% of TD. [13]

In order to improve properties of ceramics, it is desirable to achieve microstructures with nearly full density and fine grains with homogenous distribution. Along with powder

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synthesis, consolidation and shaping of the ceramic green bodies, the optimization of the sintering process has been in the focus of attention during the last couple of decades. It is well know that density has very important role on dielectric properties of magnesium titanate, especially dielectric constant.[14,15]

In this paper, the authors compared properties of magnesium titanate ceramics obtained by conventional and advanced HIP sintering technique, from mechanically activated powder mixtures. According to author's best knowledge, this is the first study of the influence of mechano-chemical activation of precursor mixture on the final density and phase purity ($MgTiO_3$).

## 2. Experimental

Commercial powders MgO (99% Sigma–Aldrich) and $TiO_2$ anatase modification (99.8% Sigma–Aldrich) were mixed in molar ratio 1:1 and milled in high energy planetary ball mill (Fritsch Pulverisette) for the time interval of 0, 10, 40, 80 and 160 minutes. Ball to powder mass ratio was 40:1 and activation was performed in air atmosphere. Balls and bowls were from $ZrO_2$. As MgO powder reacts easily with $CO_2$ and $H_2O$ which are always presented in air, the precursor was calcined at 700°C for 2h right before the milling process. The cylindrical green bodies were formed from mechanically activated powders by cold isostatic pressure at 300 MPa. The green body samples were consolidated by conventional sintering at 1400 °C with constant heating rate of 10 °C/min, dwell for 30 min and cooling rate 5 °C/min. This pressureless sintering was performed in an air atmosphere. The samples were then cut in half and post-sintered by pressure assisted technique Hot Isostatic Pressing (HIP) at 1280 °C for 3 hours in argon atmosphere with applied pressure of 200 MPa (ABRA Shirp, Switzerland). Densities of all samples were established by Archimedes method, (EN 623-2).

The morphology of obtained powders has been investigated by scanning electron microscopy (JEOL JSM-6390 LV). The pellets were cracked and covered by gold layer in order to increase the contrast during observation by SEM. Phase composition of sintered samples were determined by X-ray diffraction patterns using a Philips PW-1050 diffractometer with λCu-Kα radiation and a step/time scan mode of 0.05 °/s.

## 3. Results and discussion

For calculation of relative density the authors used the theoretical value of density (TD) $\rho_{theor}$ = 4.00 g/cm³.[16] Obtained densities as well as content of open and closed porosity are given in Tab. I.

**Tab. I** Relative and absolute densities as well as relative content of open and closed porosity of samples sintered by conventional sintering.

| Sample | Absolute density [g·cm⁻³] | Relative density [%] | Rel. open porosity [%] | Rel. closed porosity [%] |
|--------|--------|--------|--------|--------|
| MT-0 | 2.97 | 74.3 | 20.7 | 5.0 |
| MT-10 | 3.70 | 92.6 | 0.1 | 7.3 |
| MT-40 | 3.68 | 92.1 | 0.1 | 7.9 |
| MT-80 | 3.71 | 92.8 | 0.1 | 7.1 |
| MT-160 | 3.76 | 94.0 | 0.0 | 6.0 |

**Tab. II** Relative and absolute densities of samples sintered by HIP.

| Sample | Absolute density [g·cm$^{-3}$] | Relative density [%] |
|--------|--------|--------|
| MT0-HIP | 3.00 | 75.0 |
| MT10-HIP | 3.78 | 94.6 |
| MT40-HIP | 3.74 | 93.6 |
| MT80-HIP | 3.84 | 96.0 |
| MT160-HIP | 3.84 | 96.0 |

As it can be seen from Tab. I non-activated samples sintered at 1400 °C has the smallest density values, only 74.3 % of TD. In case of activated samples, values are significantly higher, in the range 92-94 % of TD. There are probably few reasons for such behavior: non-activated powder has dominantly large agglomerates of calcinated magnesium oxide, around 7 μm [17], inhomogeneity of starting powder which was mixed only manually in mortar and chemical reaction that has just begun. This sample is in medium sintering stage, (Fig. 2. a)), and relative open porosity is more than 20 %. As it is well known, mechanical activation could simplify or accelerate solid-state reaction, reducing temperatures of chemical reaction or sintering temperature.[18] In activated powders a mechanically induced energies can increase sinterability and facilitate densification. It is noticeable from Tab. I that samples MT-10 - MT-160 has negligible open porosity. Densities obtained after HIP sintering are presented in Tab. II. The above values show that samples activated for 80 and 160 minutes reached maximum of densities 96% of TD. Non-activated sample has low relative density after HIP sintering because it has great open porosity, and in that case HIP was not effective.[19] Also, it can be observed that sample MT-160 has higher values of densities before HIP than samples MT-80, but the same one after second sintering process. The main reason for such behavior could be trapping of pores in the grain interior owing to sudden grain growth during sintering at 1400 °C. Pores created this way stay even after the HIP.[19] Densities before and after HIP are graphically presented at Fig. 1, where the influence of mechano-chemical activation is clearly shown.
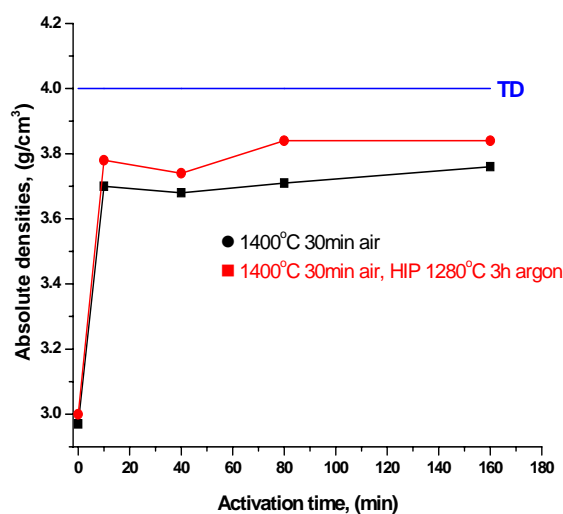


**Fig. 1.** Effect of Hot Isostatic Pressing on the sample densities.

Microstructure of sample MT-0 indicates a medium sintering stage with high amount of open porosity and presence of few different phases, which is precisely obtained by XRD. Activated samples are characterized, Fig. 2.b)-c), with closed pores which are not completely spherical in shape because starting powder consist agglomerates. Samples MT-80 and MT-160 indicate at final sintering stage with dominantly spherical pores.
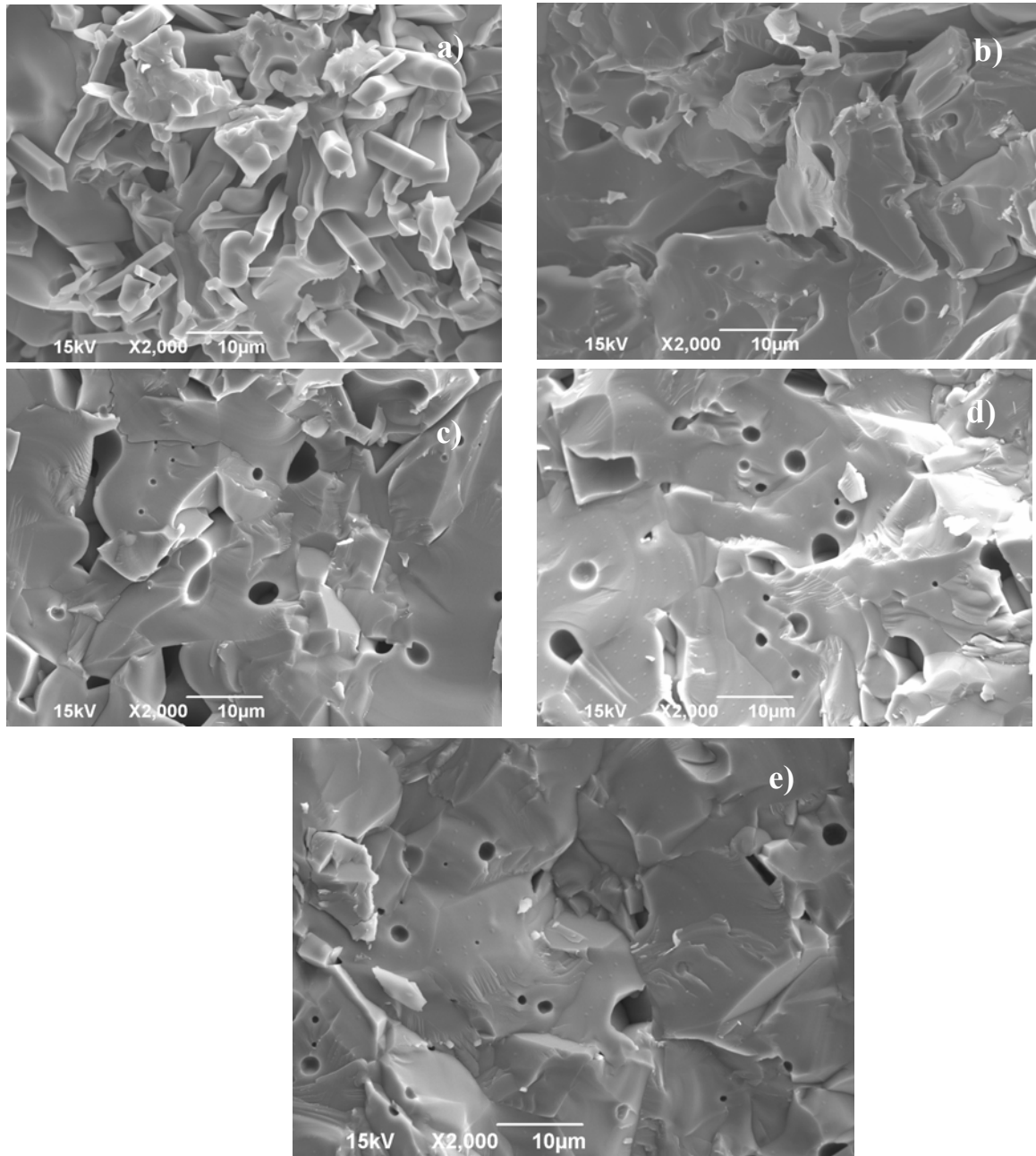


**Fig. 2.** Micrographs of samples sintered at 1400 °C 30 minutes: a) MT-0, b) MT-10, c) MT-40, d) MT-80 and e) MT-160.
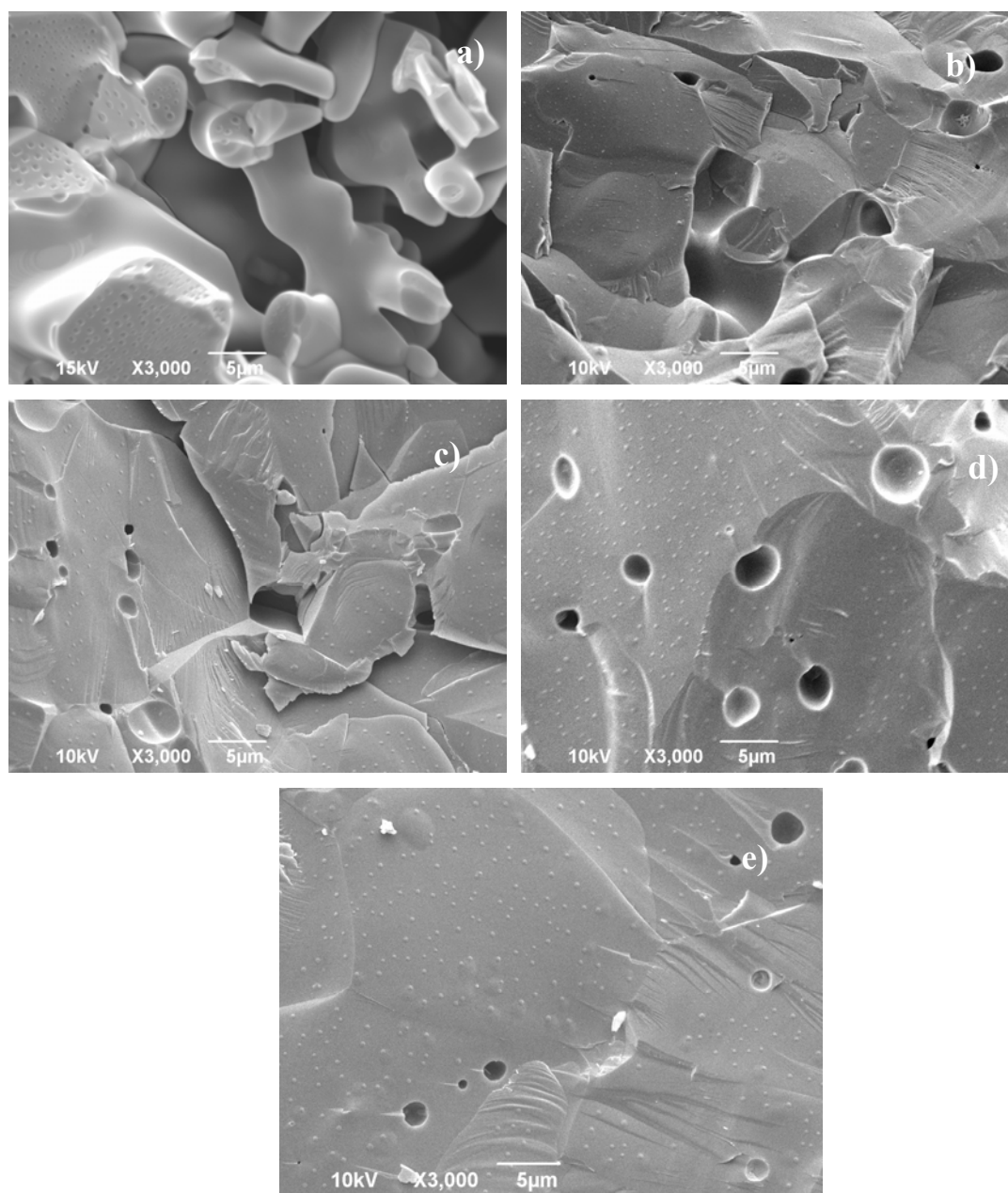
**Fig. 3.** Micrographs of samples sintered at 1400 °C for 30 minutes and post-sintered by HIP at 1280 °C for 3 hours in argon: a) MT0-HIP, b) MT10-HIP, c) MT40-HIP, d) MT80-HIP and e) MT160-HIP.

SEM picture of non-activated samples shows large open porosity. In addition, it can be noticed presence of small spherical pores due to sintering inside agglomerates that existed in the initial powder. Micrographs of samples activated for 10 and 40 minutes have dominantly closed pores but they are not completely sphere in shape, most probably due to the existence of agglomerates in starting powders. At the sites of the fracture, it is noticeable presence of the second phase. For the samples activated 80 and 160 minutes dominate compact structure along with closed spherical pores, indicating at final sintering stage. Fracture through grains can be seen.

If we compare SEM micrographs of samples sintered by conventional and HIP

sintering process, it can be concluded that combined sintering induced much more compact ceramics matrix than single stage sintering resulting in higher densities, along with smaller share of pores.
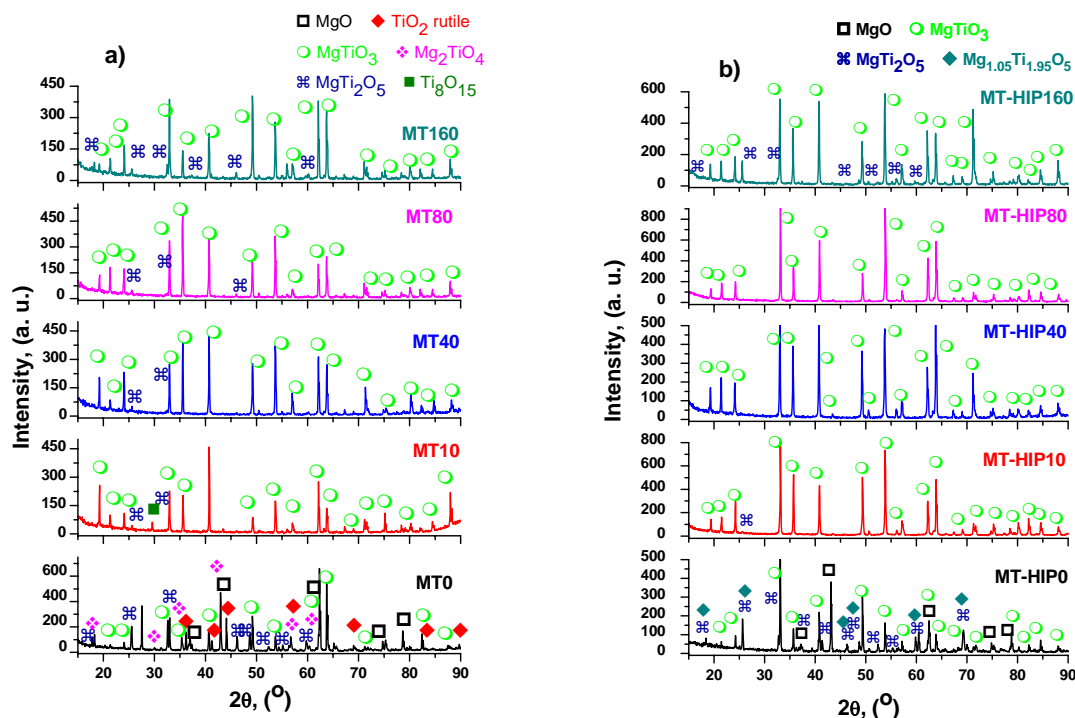


**Fig. 4.** XRD patterns of samples: a) single stage sintered (1400 °C 30 minutes), b) HIP sintered (1400 °C 30 minutes and HIP at 1280 °C for 3 hours in argon).

Fig. 4. presents XRD analysis of non activated and all activated samples sintered by two different techniques. All detected peaks were identified using JCPDS cards: 79-0831 for $MgTiO_3$, 73-1723 for $Mg_2TiO_4$, 76-2373 for $MgTi_2O_5$, 89-4920 for $TiO_2$ rutile, 87-0651 for MgO, 85-1060 for $Ti_8O_{16}$ and 52-0622 for $Mg_{1.05}Ti_{1.95}O_5$.

Diffraction patterns showed sharp and intensive reflection indicating that recrystallization process occurs during the sintering. If we observe a phase composition of samples sintered by conventional method, we can identify a few different phases. In non-activated sample, $MgTiO_3$, $Mg_2TiO_4$, $MgTi_2O_5$, $TiO_2$ rutile, MgO and $Ti_8O_{16}$ are present indicating that chemical reaction is still not finished. Activated samples are combination of $MgTiO_3$ as the dominant phase with presence of $MgTi_2O_5$ as a minor phase.

In the patterns of HIP sintered samples a $MgTiO_3$ as a dominant phase is detected along with small amount of residual phases, $MgTi_2O_5$, $Mg_{1.05}Ti_{1.95}O_5$, MgO, suggesting that chemical reaction is near completion. Furthermore, X-ray analyses of MT-HIP40 and MT-HIP80 indicate the presence of pure $MgTiO_3$ phase, which was one of the main goals of this investigation.

## 4. Conclusion

The aim of this paper was to highlight benefits of combined sintering compared to conventional sintering for magnesium titanate ceramic. Calculation of densities, by Archimedes method, showed that samples obtained from HIP sintering achieve higher values, 96% of TD for MT-HIP80 and MT-HIP160, till samples conventionally sintered has the most

94% of TD. It was determined that sample MT-160 had higher values of densities before HIP than samples MT-80, but the same one at the end of process, because trapping of pores in the grain interior. SEM micrographs showed that HIP sintering induced much more compact ceramics matrix than single stage sintering. XRD analyses confirmed that samples MT-HIP40 and MT-HIP80 are pure $MgTiO_3$ ceramic. Based on all presented facts it can be concluded that HIP sintering has better achievements contrary conventional sintering. Sample activated for 80 minutes and HIP sintered reaches almost full density and pure $MgTiO_3$, along with final sintering stage with closed and spherical pores.

## Acknowledgement

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*Садржај: У овом раду су испитане предности комбинованог процеса синтеровања, механички активиране магнесијум титанатне керамике, у поређењу са*

*конвенционалним. Стехиометријска смеша прахова MgO и TiO₂ је механички активирана у трајању од 0, 10, 40, 80 и 160 минута а потом изостатички пресована да се формирају таблете. Конвенционално синтеровање је реализовано загревањем до 1400 °C и задржавањем од 30 минута у атмосфери ваздуха. Узорци код којих је постигнута затворена порозност су подвргнути додатном ступњу топлог синтеровања под притиском на 1280 °C/3h у атмосфери аргона и под притиском од 200 MPa. Најбољи резултати су постигнути за узорке који су синтеровани под притиском, где је добијен чист MgTiO₃ релативне густине 96% од теоријске вредности.*

***Кључне речи:*** *синтеровање, керамика, магнезијум титанат.*