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Effect of Ball Milling on Reactive Microwave Sintering of MgO-TiO_2 System

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ABSTRACT

In this paper, the effect of mechanical activation on microwave reactive sintering of MgO-TiO_2 system was investigated. Mixtures of MgO and TiO_2 powders were milled at different times. The as-received mixed powder and the 10h milled mixture were sintered in microwave between 1000-1400°C. Results showed that increasing the temperature up to 1400°C for mixed powders could not give rise to complete formation of Magnesium titanate phases and unreacted raw materials were presented as the products. Also the densities of these samples were about 3 g/cm^3. With milling the reactants up to 10 h, it seems that the reactions could be completed at 1000°C and the density was augmented to 3.58 g/cm^3. Samples which have been sintered at 1400°C using a microwave furnace exhibited good microwave dielectric properties while ε_r and tan δ were 16.3 and 0.0001, respectively.

1. INTRODUCTION

Ceramic materials have significant applications in filters and resonators for communication and radar systems at microwave frequencies [1,2]. One of these materials is Magnesium titanate. Therefore MgO-TiO_2 system has been investigated extensively.

Obtaining pure $MgTiO_3$ is difficult when using solid-state reactions because some metastable titanate phases were formes during the reaction [3]. For synthesis of pure $MgTiO_3$, Mg:Ti ratio should be kept at 1, which can be achieved by mixing the raw materials homogeneously [3].

There are three phases in this system, $MgTiO_3$, Mg_2TiO_4 and $MgTi_2O_5$. The structures are illmenite, pseudobrookite and inverse spinel, respectively [4]. Formation temperature of $MgTiO_3$ is above the 600°C and it is stable at room temperature up to its melting point [5,6]. The Mg_2TiO_4 is formed at temperatures above the 1150°C and undergos a phase transition in the cooling process at 1000◦C to a tetragonal modification [7]. $MgTiO_3$ (MT) was reported to exhibit good dielectric properties of $\varepsilon_r \sim 17$, $Q \times f \sim 160{,}000$ at 7 GHz and $\tau_f \sim -50$ ppm/◦C. Dielectric properties of $MgTi_2O_5$ are $\varepsilon_r \sim 17.4$, $Q \times f \sim 47{,}000$ GHz and $\tau_f \sim -66$ ppm/°C [8]. Also dielectric constant and $Q \times f$ of Mg_2TiO_4 were reported about 14.4 and 55000, respectively [9].

Different methods have been reported for synthesis of $MgTiO_3$. The first synthesis of $MgTiO_3$ was in 1864 which has been synthesized from magnesium chloride, ammonium chloride and titanium oxide by calcination at 900◦C [10]. The $MgTiO_3$ is usually synthesized by solid state reaction at the 1400◦C [11]. As diffusion is a significant stage in the solid state reaction, mechanical activation could accelerate solid state reaction or reduce the reaction temperature. High energy ball milling is a simple method for preparing nanomaterials. It has many advantages such as simplicity and low cost which make it applicable to any class of materials [12]. Milling treatment is understood to enhance the powders reactivity so it can be called Mechanical Activation (MA) [13,14]. Dependent on the intensity of milling condition (milling time, ball to powder ratio, etc.) chemical and structural changes can be induced in the systems. MA can change thermodynamic potentials of materials and short lenght diffusion so decreases the temperature of chemical reaction [15]. There are not many papers about effect of mechanical activation on microwave sintering of MgO-TiO_2 system, but in a few papers the effect of mechanical activation on conventional sintering of this system was ivestigated [11]. They showded that in all of the sintered samples, mixtures of $MgTiO_3$ and $MgTi_2O_4$ were present. In another study [3] wet milling was used for the synthesis of pure $MgTiO_3$, however the sintering was not investigated.

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In this paper we investigated the effect of mechanical activation on microwave sintering of MgO-TiO_2 system.

2. EXPERIMENTAL PROCEDURES

MgO (Merck) and TiO_2 (S.D. Fine Art: 40446,<44 μm, 98% purity) powders were used as starting materials. A molar ratio of 1:1 for TiO_2:MgO was weighted and mixed. The mixure was mechanically milled for 0, 3, 6 and 10 h in a stainless steel container and balls using 200 rpm with 10:1 ball to powder ratio (denoted as MT0, MT3, MT6 and MT10). The contamination during milling was characterized by ICP (ARL 3410).

MT0 and MT10 powders were compacted at 250 MPa using a cylindrical mold of 10 mm in diameter and height. The sintering of the samples was carried out in a microwave oven between 1100- 1400°C. Phase composition of the milled powders and bulk products were investigated by X-ray Diffraction (Philips PW 3710) using Cu-Kα radiation (λ= 0.154 nm). The morphology of calcined powders and sintered samples was characterized by SEM (Stereo Scan S360) and FE-SEM(Vega Tescan) techniques.

Densities of the samples were measured by Archimedes' method (ASTM 373). The dielectric properties at 10 GHz frequency were measured by network analyzer (HP8510C) with cavity perturbation method.

3. RESULT AND DISCUSSION

Figure 1. shows the XRD patterns of the samples milled at different times. Peaks of raw materials (MgO and TiO_2) are distinguishable for all times. It can be seen that there is no noticeable difference between the XRD patterns of these milled powders. But in the study of Filipovic et al. [11], because more severe milling conditions were applied, some other products were present in the XRD patterns of the milled powders.

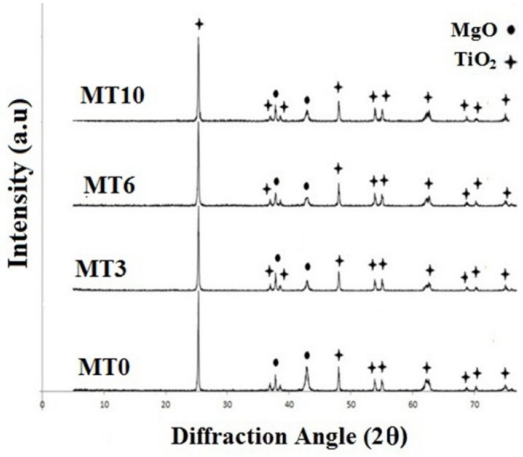

Figure 1. XRD patterns of reactants at different milling times.

On the other hand, SEM images of these powders (Figure 2.) show reduction of particles size to less than 500 nm along with the changein morphology of the powders as a consequence of milling procedure. It can be seen that the initial MgO-TiO_2 powders are irregular and flake-like shaped that are transformed to rounded-shaped as a consequence of milling. Iron contamination during the ball milling was characterized by ICP. It was sufficiently at low levels, i.e. 0.24%, for the case of 10 h milled sample.

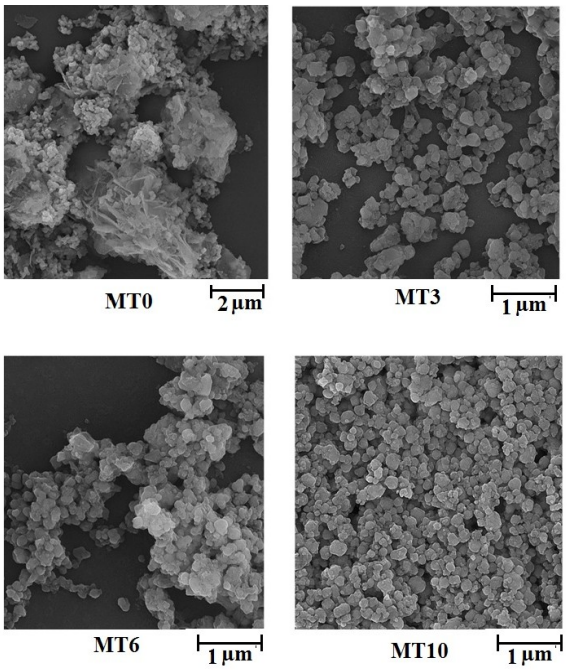

Figure 2. SEM images of reactants at different milling times.

For investigating the effect of mechanical activation on phase evolution during sintering, MT0 and MT10 powders were chosen for microwave sintering. These samples were sintered at the 1000, 1200 and 1400°C. XRD patterns of bulk samples prepared from unmilled powders and 10 h milled powders are shown in Figures. 3 and 4, respectively. In the case of unmilled powders it can be seen that at sintering temperature of 1000°C, the main phases are raw materials (MgO and TiO_2), also $MgTiO_3$ and $MgTi_2O_5$ are secondary phases. However, With increment of temperature to 1200°C and furthermore to 1400°C, products ($MgTiO_3$ and $MgTi_2O_5$) are the main phases and intensity of their peaks have been increased, also peaks related to MgO and TiO_2 still exist. It can be concluded that by using as-received reactant (unmilled powder), formation of Magnesium titanate could not be completed even up to temperature of 1400°C. Formation of $MgTiO_3$ was completed at 1000°C and only increase of temperature gives rise to the increment of $MgTiO_3$ and $MgTi_2O_5$ crystalinity. Regarding the results, the reaction for synthesis of $MgTiO_3$ approaches the completion at

lower temperature levels when starting by 10 h milled powders (1000℃) as compared to the case of as-received reactants (more than 1400℃). This shows the importance of interface formation between reactants which is induced by milling process to enhance diffusion, and consequently chemical reactions. As milling process proceeds, powders size is decreased and interfacial surfaces between reactants is progressively promoted. Both of these features help the mass transport by diffusion and therefore, by occurrence of reactive microwave sintering.

The densities of the unmilled powder prepared at 1400°C (MT0M-1400), powder milled for 10h at 1200°C (MT10 M-1200) and the powder milled for 10h at 1400°C (MT10M-1400) by microwave furnace were measured. It can be seen that (Table 1) due to reduction of particles size and increase of driving force for sintering, milling of reactants up to 10 h gives rise to increase in density from 3 to 3.58g/Cm^3. Although milling of reactants induces anincresae in density values, if we assume that the only phase is $MgTiO_3$, the relative density would be about 92%.

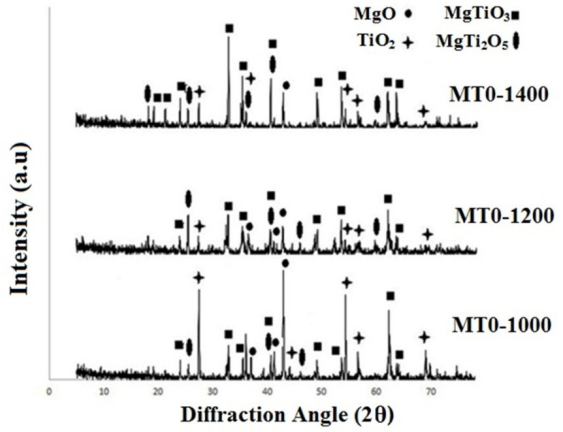

Figure 3. XRD patterns of unmilled reactants sintered at different temperatures.

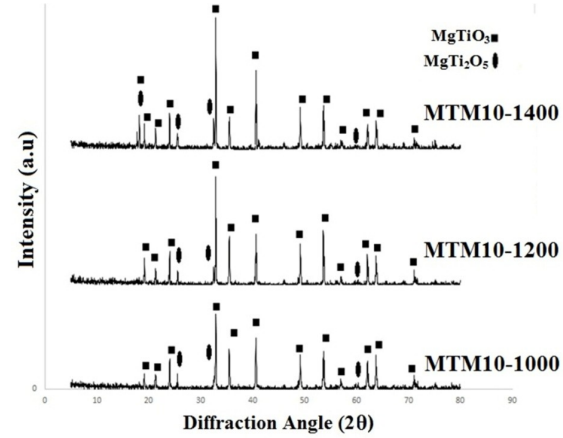

Figure 4. XRD patterns of 10 h milled reactants sintered at different temperatures.

TABLE 1. Density values and dielectric properties of the samples.

Sample	Density (g/cm^3)	ε_r	Tanδ	Q	Q.F (GHz)
T0 M- 1400	3.00	15.8	0.00021	4761	47619
T10M-1200	3.42	16.1	0.00013	7692	76923
T10M-1400	3.58	16.3	0.0001	10000	100000
4T10F-1400	3.6	16.7	0.0001	10000	100000

Also for comparing and understanding the effect of microwave sintering, MT10 sample was sintered in an ordinary furnace at 1400℃ for 2h (MT10F-1400) (Table 1). It can be seen that there are no noticeable differencesamong the density values. Also the related XRD patterns are shown in Figure 5. and proves that they have almost the same compositions. Microstructures of these two samples (MT10M-1400 and MT10F-1400) are shown in Figure 6. It can be seen that there are not any differences regarding the shape of the grains but grains of the sample sintered in microwave furnace possess higher aspect ratios. Different parameters are proved to influence the quality factor that can be divided in two sections: 1) Intrinsic loss and 2) Extrinsic loss. Lattice vibration modes cause intrinsic loss, and second phase, oxygen vacancies, grain sizes and porosity are related to extrinsic loss [16].

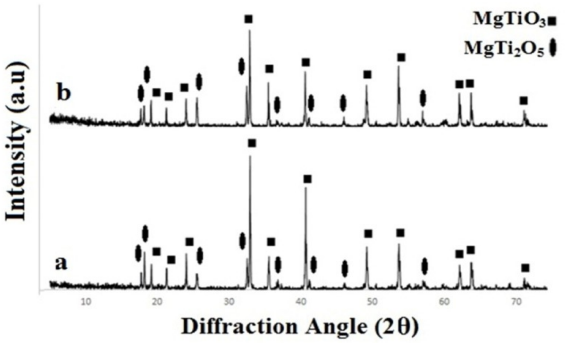

Figure 5. XRD patterns of 10 h milled reactants sintered at 1400℃ in (a) microwave furnace, and (b) ordinary furnace.

In this study, due to reaction sintering, the samples densities are lower than that of the samples reported in literature [17-18]. It is worthy to be mentioned that other researchers used conventional sintering and other powder synthesis procedures. For exmaple Wu et al. [17] has sintered the obtained $MgTiO_3$ podwer via sol-gel method with εr = 17.5 and Q×f =156300 GHz or Mia et al. [18] reporetd Qf value of 42600GHz using the organic sol gel method.

Also it was found that relative density is one of the most important factors determining the dielectric loss. In this study because of low density and stability of $MgTi_2O_5$

that possesses a low Qf in comparison to $MgTiO_3$, the quality factors are low.

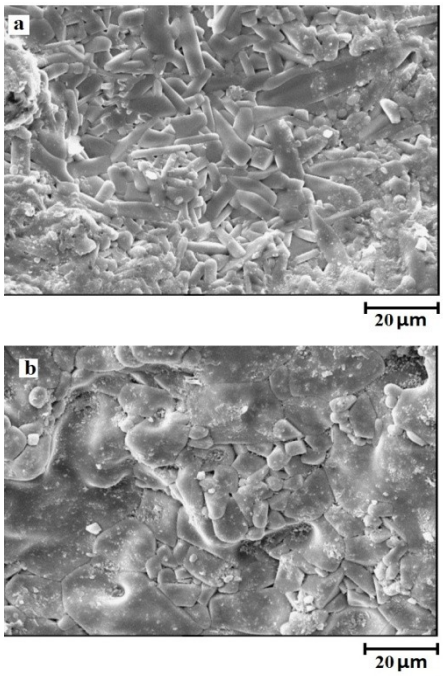

Figure 6. SEM images of 10 h milled reactants sintered at 1400℃ in (a) microwave furnace, and (b) ordinary furnace.

4. CONCLUSION

Microwave sintering of MgO–TiO_2 system on unmilled mixtures and the mixtures milled for 10 h was investigated. In the case of unmillled powders, even after sintering the samples at 1400℃ peaks realted to raw materials could be distinguished in XRD patterns. In the other words, the reaction cannot be completed; also the density was 3 g/cm^3. Milling the sample gives rise to completion of reactions at low temperature of 1000℃ and increase in density to 3.58g/cm^3 at temperature of 1400℃ which is resulted by particles size reduction. This sample showed proper dielectric properties. Also it is worth to mention that it is not possible to obtain pure $MgTiO_3$ by using this procedure even after mechanical activation of the reactants. The reason for that might be the difficulty of obtaining Mg:Ti molar ratio of 1 in this procedure.

5. ACKNOWLEDGMENTS

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