ACERP: Vol. 4, No.1, (Winter 2018) 40-44

Advanced Ceramics Progress

Research Article

Journal Homepage: www.acerp.ir

Synthesis of $MgTiO_3$ Powder Via Co-Precipitation Method and Investigation of Sintering Behavior

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P A P E R I N F O

Paper history:
Received 29 May 2018
Accepted in revised form 21 August 2018

Keywords:
Magnesium Titanate
Co-Precipitation
Microwave Dielectric
Sintering

A B S T R A C T

A co-precipitation method was used for synthesis of pure $MgTiO_3$ ceramic powder with $Mg(NO_3)_2.6H_2O$, $TiCl_4$ or $C_{12}H_{28}O_4Ti$ and NaOH as raw materials. In this method, solutions of 1 M, Mg $(NO_3)_2$ $6H_2O$ and 2 M, NaOH were prepared. A stoichiometric amount of Ti precursors from $TiCl_4$ or $C_{12}H_{28}O_4Ti$ was weighted. Solutions of Mg $(NO_3)_2$. $6H_2O$ and Ti precursor were added dropwise to NaOH solution under stirring.. The gelatinous white precipitate was calcinated at temperature range of 500-1000 °C. Moreover, the sintering process was performed at temperature range of 950-1350 °C. The results show that in the presence of $TiCl_4$, pure $MgTiO_3$ does not form, but using $C_{12}H_{28}O_4Ti$, pure $MgTiO_3$ with particle size less than 200 nm obtains at calcination temperature of 800 °C. Thus, the density of this sample is optimum (95% relative density) at a sintering temperature of 1050 °C and it has good dielectric properties including ε_r =16.2 and Q×f= 110000 GHz.

1. INTRODUCTION

$MgTiO_3$ (Magnesium Titanates) has noticeable applications in several aspects like chips, high frequency temperature compensating capacitors, resonators, filters and antennas for communication and millimeter wave frequencies [1-3]. It has dielectric properties with high quality factor (Q above 20000 at 8 GHz), appropriate (intermediate) dielectric constant ($\varepsilon_r \approx 17$) and near zero temperature coefficients (τ_f) [4]. In order to control its dielectric properties (Q, ε_r and τ_f), it is necessary to produce $MgTiO_3$ powders with very high purity, proper morphology and narrow distribution of the particle size [5]. As have been reported in most studies, in the synthesis of $MgTiO_3$, other magnesium titanates ($MgTi_2O_5$ and Mg_2TiO_4) are formed especially in solid-state reaction [6]. However, only a few studies have been obtained pure $MgTiO_3$, as most of them have been applied complex ways. These ways make delay in shrinkage and sintering processes by producing special phases along with modification in the dielectric properties of the materials [6].

The synthesis of $MgTiO_3$ has been carried out using different methods such as solid-state reaction [6-7], thermal decomposition of peroxide [8], hydrothermal mechanical- chemical complexation [9], organic and aqueous sol-gel [10-14], chemical co-precipitation [15-17] and the other methods [18-21]. Co-precipitation is one of the most suitable techniques for the synthesis of ultrafine powder with narrow distribution of the particle size. This process is a simple method that consumes less time in comparison with the other techniques [15]. To the best of our knowledge, only few studies have been carried out regarding using co-precipitation method in the preparation of $MgTiO_3$. For example, Cheng et al. [16] have used $Ti(SO_4)/Mg(SO_4)$ and NaOH solutions as precursors. They have concluded that in order to synthesize pure $MgTiO_3$, it is necessary to maintain the pH of the reaction greater than 12 through the addition of NaOH solution. In another study [17], $MgTiO_3$ sample was prepared using co-precipitation method through the reaction of $Ti(OH)_4$ + $Mg(NO_3)_26H_2O$ $\rightarrow MgTiO_3 + NH_4NO_3 + H_2O$, which was carried out at 1000K for 8 h. Furthermore, in a research conducted by Gaikwad et al. [15], $Mg(NO_3)_2.6H_2O$ and $TiOCl_2$ were used as precursors for Mg and Ti. Moreover, ammonium hydroxide and ammonium carbonate were served as precipitation agents. In all three aforementioned cases, pure $MgTiO_3$ was obtained, but none of them has been studied the sintering behavior.

The purpose of this study is to synthesize pure $MgTiO_3$ powder using co-precipitation method and investigate their sintering behavior and dielectric properties.

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2. EXPERIMENTAL PROCEDURES

2.1. Synthesis method

The high purity raw materials (from Merck Company) used in current research are listed in Table 1.

TABLE 1. The chemical composition of starting materials

Company	Formula	Raw Materials
Merck	$Mg(NO_3)_26H_2O$	Magnesium Nitrate
Merck	$TiCl_4$	Titanium chloride
Merck	NaOH	Sodium hydroxide
Merck	$C_{12}H_{28}O_4Ti$	Titanium Isopropoxide

In order to obtain $MgTiO_3$, aqueous solutions of 1M Mg $(NO_3)_2$. $6H_2O$ and 6M NaOH were prepared. As a result of the high chemical reactivity of Titanium Isopropoxide (TTIP) with water, it was used without being dissolved in water. After preparing the solutions, another $Mg(NO_3)_2.6H_2O$ solution TTIP were added dropwise to the NaOH solution simultaneous with vigorous stirring for about 30 min. During the experiment, the pH of the reaction was kept greater than 12 by adding NaOH solution to ensure complete precipitation. AdditionallyTTIPwas replaced with $TiCl_4$. In both experiments, precipitates were collected via filtration and washed three times with distilled water and absolute ethanol in order to remove residual ions. Finally, the precipitates were dried at 60 °C. Thereafter, the powders were calcinated at a temperature between 600 and 1000 °C for 2 h. The calcinated powders were mixed with PVA binder, granulated and compacted in a cylindrical disk with dimensions of 10 mm in diameter and 4 mm in height with a pressure capacity of 250 MPa. As a final point, green compacts were sintered at 950-1150 °C for 2 h in air.

2.2. Materials characterization

For analysis and evaluation of phases, the as-formed precipitate was characterized using DTA (Polymer Laboratories, STA-1640). DTA was performed in air atmosphere with alumina reference sample, using a heating rate of 10 °C/min. The phase composition of the synthesized powders and bulk products were investigated by X-ray diffraction (Philips PW 3710) using Cu Kα radiation(λ= 0.154 nm). The morphology of calcinated powders and sintered samples was characterized by SEM (Stereo ScanS360 and Vega Tescan). The sample densities were measured using the Archimedes rule according to the C-373 ASTM standard. The dielectric properties at 10 GHz frequency were measured via network analyzer (HP8510C) with cavity perturbation method.

3. RESULT AND DISCUSSION

Fig. 1(a) shows the XRD patterns of the precipitate when $TiCl_4$ was used as Ti precursor, before and after the calcination process.

It can be seen that the precipitate is composed of crystalline $Mg(OH)_2$ and amorphous substances of (TiO_2. XH_2O). Since the calcination temperature of the $MgTiO_3$ powder (MT) has been reported between 500-1000 °C [8-11], so, the calcinations process was implemented at a temperature more than 1000 °C. Fig. 1(b) and 1(c) show the phase composition of calcinated powder at 1000 and 1200 °C. $MgTiO_3$ and Mg_2TiO_4 peaks are distinguishable, while at 1000 °C, the peaks of Mg_2TiO_4 are sharper than $MgTiO_3$. However, when the temperature increases to 1200 °C, the peak of $MgTiO_3$ becomes sharper, indicating that an increase in temperature results in the transformation of Mg_2TiO_4 to $MgTiO_3$. Thus, it seems that with this procedure, pure MT products cannot be synthesized.

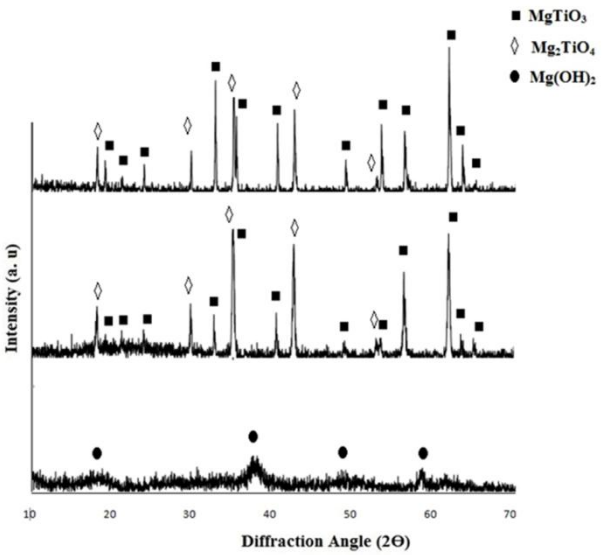

Figure 1. The XRD patterns of the obtained products by using $TiCl_4$ as the Ti precursor: a) after co-precipitation and after the heat treatment at the temperatures of b) 1000 °C and C) 1200 °C

Cheng et al. [15] have observed that the parameters such as Mg:*Ti* molar ratio in the raw materials, the pH of the reaction and the type of precipitating agent have significant effect on the phases and products. Besides, they have concluded that for the synthesis of pure $MgTiO_3$ with mixed solution of $Ti(SO_4)_2/Mg(SO_4)$ and NaOH, it is essential to maintain pH greater than 12 in the reaction by adding NaOH solution. This is because of that the sedimentation of Mg^{+2} and Ti^{+4} ions could be performed simultaneously when Ti^{+4} and Mg^{+2} precipitation occurs at pH 7-8 and pH-12, respectively. Although in this study, pH manipulation of the reaction was fulfilled through the addition of NaOH, however,

the synthesis of pure MT products was impossible. Nevertheless, when the $TiCl_4$ become more volatile, obtaining a homogenously mixed solution of Mg and Ti ions become difficult, because of the problems associated with its handling and working. Therefore, $TiCl_4$ was replaced with TTIP and co-precipitation was carried out.

For evaluating composition during heat treatment of the precipitant, DTA test was conducted for the samples that TTIP was used as Ti precursors. Fig. 2 shows the DTA-TG curves of precipitate obtained from TTIP known as the Ti precursor. The first and second endothermic peaks at 118 °C and 361°C (with 30% mass loss) correspond to the dehydration of the precursors and decomposition of $Mg(OH)_2$, respectively, as shown in Reaction 1:

$$Mg(OH)_2 \rightarrow MgO_{(s)} + H_2O_{(g)} \quad (1)$$

The first exothermic peaks at 500-700 °C together with 3% mass loss corresponds to the formation of $MgTiO_3$ and Mg_2TiO_5 phases. It can be seen that after 700 °C, there was no clear mass loss [5 ,18].

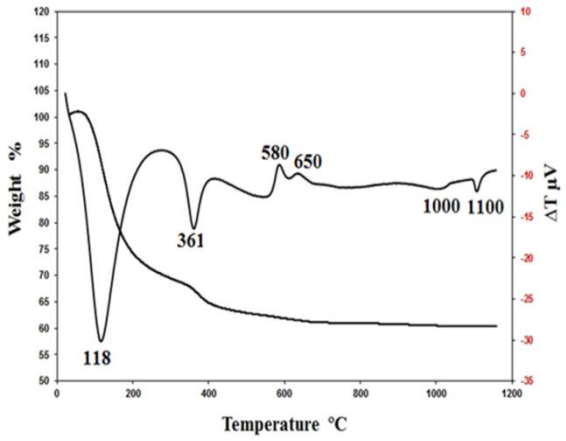

Figure 2. The curve of TG/DTA for precipitate by using TTIP as the Ti precursors

To evaluate the phase composition during thermal treatment, XRD patterns of synthesized powder along with calcinated powders between 500-1000 °C are shown in Fig. 3. It can be seen that the synthesized powder is amorphous in nature and there are no peaks in its pattern (Fig. 3(a)). As temperature increases to 500 °C, MgO and TiO_2 are crystallized from the synthesized amorphous powder. Moreover, the peaks related to the nucleus of $MgTi_2O_5$ and Mg_2TiO_4 can be distinguished. At 600 °C, there is an increase in the intensity of $MgTi_2O_5$ phase along with some peaks, which correspond to the $MgTiO_3$ phase. There is no significant difference between the XRD patterns of calcinated powders at 700 °C and 600 °C, but an increase in the intensity of the peaks related to the $MgTiO_3$ phase is sensible. By increasing the calcination temperature to 800 °C, the $MgTi_2O_5$ peaks diminishes and the $MgTiO_3$ peaks becomes sharp, which is a sign of the transformation from $MgTi_2O_5$ to $MgTiO_3$. It can be concluded that the pure $MgTiO_3$ phase can be obtained at calcination temperatures above 800 °C. However, above 800 °C, the $MgTiO_3$ peaks are sharp, so, the grain coarsening can be occurred that confirms by microstructure investigation.

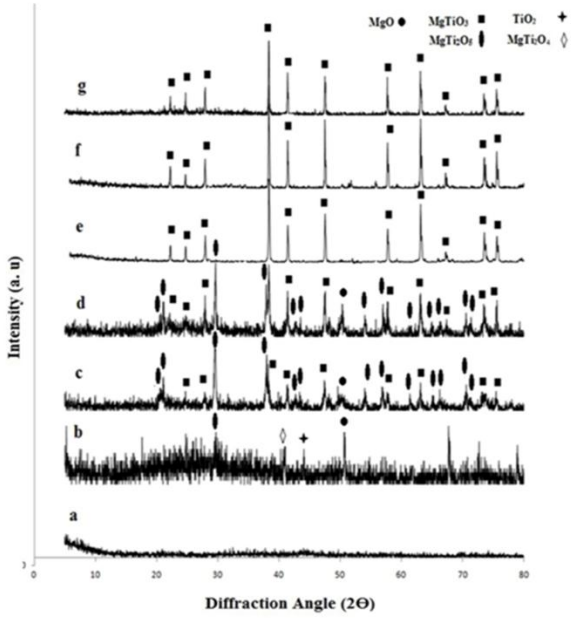

Figure 3. The XRD patterns of the obtained products by using TTIP as the Ti precursor: a) after co-precipitation and after the heat treatment at the temperatures of: b) 500 °C, c) 600 °C, d) 700 °C, e) 800 °C, f) 900 °C. and g) 1000 °C

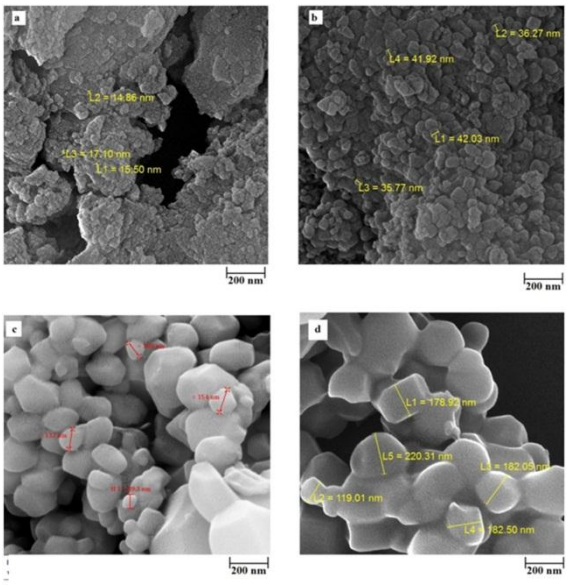

Figure 4. The SEM images of the obtained products by using TTIP as the Ti precursor a) after co-precipitation and after the heat treatment at the temperature of b) 500 °C, c) 600 °C, d) 700 °C, e) 800 °C, f) 900 °C. and g) 1000 °C

Fig. 4 shows the microstructure of calcinated powders obtained by SEM. It can be seen that the synthesized amorphous powder is a nano particle with size of less than 20 nm (Fig. 4(a)). When the calcination temperature arises to 700 °C, then the particle size increases to 30-40 nm (Fig. 4(b)). It is worthy to note that the particle size is less than 200 nm at calcination temperatures of 800 °C and 1000 °C (Figs. 4(c) and 4(d)). These images confirm the XRD results.

After calcinations at a calcination temperature of 800 °C, the powders were sintered at a temperature between 950 and 1350 °C. The data associated with the influence of temperature on the density of end–products are summarized in Fig. 5. According to the Fig. 5, when the temperature arises, at first, the density significantly increases. It reaches a maximum value (95% TD) when the temperature is 1050 °C and at that point decreases. Therefore, it can be determined that 1050 °C is the optimum temperature for sintering, which can be cofired with 30Pd/70Ag electrode materials [20].

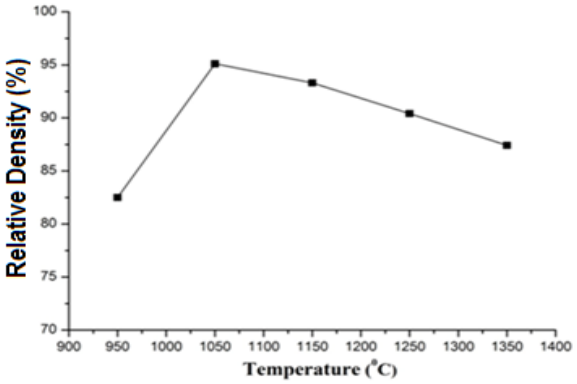

Figure 5. The effect of the temperature on the relative density of bulk products

The microstructures of the sintered samples at temperatures of 950, 1050 and 1150 °C are shown in Fig. 6. It can be easily realized that an increase in temperature leads to a growth in the grain size. The dielectric properties of this sample were suitable, as the dielectric constant and Q×f were 16.2 and 110000 GHz, respectively. These results are comparable to the other references. (Table 2)

TABLE 2. Comparison of this study with other references

Ref	Typ of synthesis	Sintering Temperature(^{0}C)	RD (%)	ε_r	Q×f (GHz)
12	Sol-gel	1200	98	16.6	42600
13	Sol-gel	1200	95	17.8	156300
21	combustion	1200	98	16.7	73700
23	chemical	1350	96.8	17.4	208333
This study	Co-precipitation	1050	95	16.2	110000

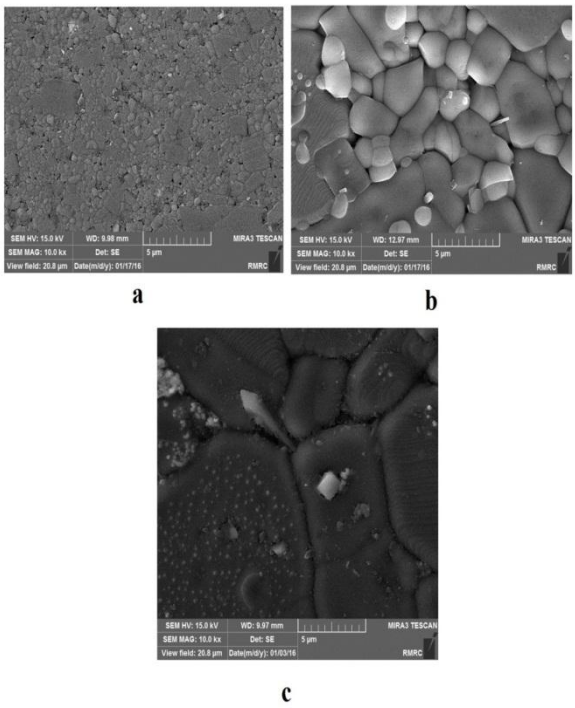

Figure 6. The SEM images of the bulk products at the temperatures: a) 950 °C, b) 1050 °C and c) 1150 °C

4. CONCLUSION

$MgTiO_3$ nanoparticles with high purity were successfully obtained using co-precipitation method and heat treated at a temperature of 800 °C. In this research, TTIP was used as precursor for Ti. Moreover, decreasing the sintering temperature to 1050 °C and reaching a good relative density (about RD=95%) were due to excellent sinterability of the powders. This sample exhibited proper microwave dielectric properties including ε_r= 16.2 and Q×f= 110000 GHz, which can be co-fired with 30Pd/70Ag and used for the preparation of subminiature multilayer components.

Milling process and microwave sintering improved mechanical and electrical properties of samples؛ the microhardness of samples milled for 1 and 30 h and sintered at 1390°C increased from 546±28 to 1089±51 Hv in microwave sintering and from 498±23 to 818±52 HV in conventional sintering, respectively.

5. ACKNOWLEDGMENTS

The authors are grateful to acknowledge the Iranian national science foundation for financial support during this project.

REFERENCES

1. Bernard, J., Houivet, D., El Fallah, J., "$MgTiO_3$ for Cu base metal multilayer ceramic capacitors", ***Journal of the European Ceramic Society,*** Vol. 24, (2004), 1877-1881.

2. Belnou, F., Bernard, J., Hoivet, D., "Low temperature sintering of $MgTiO_3$ with bismuth oxide based additions", ***Journal of the European Ceramic Society,*** Vol. 25, (2005), 2785-2789.
3. Sebastian, M.T., Dielectric Materials for wireless application., (2008), Elsevier, Amesterdam.
4. Huang, C.L., Chen, Y.B., Lee, M.L., "Influence of ZnO additions to 0.96 $Mg_{0.95}Co_{0.05}TiO_3$ –0.04 $SrTiO_3$ ceramics on sintering behavior and microwave dielectric properties", ***Journal of Alloys and Compounds,*** Vol. 469, (2009), 357-361.
5. Kang, H., wang, L., Xue, D., "Synthesis of tetragonal flake like magnesium titanate nano crystallites", ***Journal of Alloys and Compounds,*** Vol. 460, (2008), 160-163.
6. Bernard, J., Belnou, F., Houivet, D., "Synthesis of pure $MgTiO_3$ by optimizing mixing/grinding condition of MgO + TiO_2 powders", ***Journal of Materials Processing Technology,*** Vol. 199, (2008), 150-155.
7. Tang, B., Zhang, S., Zhou, X.H., "Preparation of pure $MgTiO_3$ powders and the effect of the $ZnNb_2O_6$-dope onto the property of $MgTiO_3$-based ceramics", ***Journal of Alloys and Compounds,*** Vol. 492, (2010), 461-465.
8. Pfaff, G., "Peroxide route for synthesis of magnesium titanate powders of various compositions", ***Ceramics International,*** 1994, **20**:111-116.
9. Baek, J.G., Isobe, T., Senna, M., "Mechanochemical Effects on the Precursor Formation and Microwave Dielectric Characteristics of $MgTiO_3$", ***Solid State Inonics,*** Vol. 90, (1996), 269-279.
10. Surendran, K.P., Wu, A.Y., Vilarinho, P.M., "Sol−Gel Synthesis of Low-Loss $MgTiO_3$ Thin Films by a Non-Methoxyethanol Route", ***Chemistry of Materials,*** Vol. 20, (2008), 4260-4267.
11. Rajesh Kanna, R., Dhineshbabu, N., Paramasivam, R., "Synthesis of Geikielite ($MgTiO_3$) Nanoparticles via Sol–Gel Method and Studies on their Structural and optical properties", ***Journal of Nanoscience and Nano Technology,*** Vol. 16, (2016), 7635-7641.
12. Miao, Y.M., Zhang, Q.L., Yang, H., "Low-temperature synthesis of nano-crystalline magnesium titanate materials by the sol–gel method", ***Materials Science and Engineering B,*** Vol. 128, (2006), 103-106.
13. Wu, H.T., Jiang, Y.S., Cui, Y.J., "Improvement in sintering behavior and microwave dielectric properties of giekielite type $MgTiO_3$ Ceramics", ***Journal of Electronic Materials,*** Vol. 42, (2013), 445-451.
14. Li, D., Wang, L., Xue, D., "Strearic acid gel derived $MgTiO_3$ nanoparticles: a Low temperature intermediate Phase of Mg_2TiO_4", ***Journal of Alloys and Compounds,*** Vol. 492, (2010), 564-569.
15. Gaikwad, A.B., Navale, S.C., Samuel, V., "A co- precipitation technique to prepare $BiNbO_4$, $MgTiO_3$ and $Mg_4Ta_2O_9$ powders", ***Materials Research Bulletin,*** Vol. 41, (2006), 347-353.
16. Cheng, H., Xu, B., Jiming, M.A., "Preparation of $MgTiO_3$ by an improved chemical co-precipitation method" The Journal of Materials Science, Vol. 16, (1997), 1570-1572.
17. Parthasrathy, G., Manorama, S.V., "A novel method for synthesizing nano-crystalline $MgTiO_3$ geikielite", ***Materials Research Bulletin,*** Vol. 30, (2007), 19-21.
18. Deng, Y.F., Tang, S., Qiang, D., Lao, L., "Synthesis of magnesium titanate nanocrystallites from cheap and water-soluble single source precursor", Inorganica Chimica Acta, Vol. 363, (2010), 827-829.
19. Stubicar, N., Tonjec, A., Stubicar, M., "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,*** Vol.370, (2004), 296-301.
20. Hamada, K., Yamamoto, S., Senna, M., "Effects of milling raw materials and slurry concentration on the synthesis of magnesium titanate", ***Advanced Powder Technology ,*** Vol. 11, (2000), 361-371.
21. Suresh, M.K., Thomas, J.K., Sreemoolanadhan, H.C., "Synthesis of nanocrystalline magnesium titanate by an auto-ignition combustion techniqure and its structural, spectrospic and dielectric properties", ***Materials Research Bulletin,*** Vol. 45, (2010) 761-765.
22. Wang, H., Yang, Q., Li, D., "Sintering behavior and microwave dielectric properties of $MgTiO_3$ ceramic doped with B_2O_3 by sol-gel method", ***Journal of Materials Science and Technology,*** Vol. 28, (2012), 751-755.
23. Ferreira, V.M., Baptista, J.L., Preparation and microwave dielectric properties of pure and doped magnesium titanate ceramic, ***Materials Research Bulletin,*** Vol. 29, (1994), 1017-1023.