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Synthesis of $MgTiO_3$ by solid state reaction and characteristics with addition

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Abstract Magnesium titanate was synthesized by the solid state reaction. Powder XRD method was used to identify the phases and content, which indicates that pure phase of $MgTiO_3$ can be synthesized by the solid state reaction even without the addition of excess MgO. Doped with 5 at.% $CaTiO_3$ and 6 wt.% $ZnNb_2O_6$, $MgTiO_3$ ceramics sintered at 1300 °C possess excellent microwave dielectric properties: a dielectric constant ε_r of 21, a τ_f value of 0 ppm/°Cand a Q × f value of 130,000 GHz (at 13 GHz).

Introduction

Development of microwave dielectrics having high Q values at a frequency above 10 GHz is very important for the application of new media, such as satellite communication and broadcasting systems. Thus, a number of these materials have been investigated and developed.

Magnesium titanate, with ilmenite structure, is potential material for low-loss microwave dielectric resonator application [1]. The dielectric properties are known to depend strongly on the microstructure factors such as second phases, porosity as well as microstructural factors, including lattice defects, impurities, order–disorder phenomena, and so on. Thus, these parameters have to be controlled by appropriate synthesis and processing conditions to get reliable dielectric characteristics. Synthesis of $MgTiO_3$ phase by the conventional solid-state method, by reacting individual oxide components in the appropriate molar ratios, generally results in the required corundum type $MgTiO_3$ phase, accompanied with a minor amount of a second phase ($MgTi_2O_5$) [2]. Hence, sol–gel and co-precipitation methods are often employed to achieve phase pure $MgTiO_3$ [3, 4]. However, the chemical process often requires an expensive and time-consuming flexible process. In this paper, synthesis of phase pure $MgTiO_3$, using solid-state method by introducing magnesium carbonate basic pent hydrate $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ and titanium oxide TiO_2 as the stating materials, is reported.

$MgTiO_3$–$CaTiO_3$ (abbreviated to MCT) ceramics are well known as the materials for temperature compensating type capacitor, dielectric resonator and patch antenna [2]. MCT powder is often made of a mixture of modified α-Al_2O_3 structured magnesium titanate ($MgTiO_3$: a dielectric constant ε_r of 21, a τ_f value of –50 ppm/°Cand a Q × f value of 160,000 GHz at 13 GHz) and perovskite structured calcium titanate ($CaTiO_3$: a dielectric constant ε_r of 170, a τ_f value of 800 ppm/°C and a Q × f value of 3600 GHz at 7 GHz). With the ratio Mg:Ca = 95:5, 0.95 $MgTiO_3$–0.05$CaTiO_3$ (abbreviated to 95MCT) ceramic gives $\varepsilon_r \sim 21$, Q ~ 8000 GHz at 7 GHz, and a zero τ_f value [5]. However, it requires sintering temperature as high as 1400–1450 °C. Many researchers have made efforts to study the microstructures and the microwave dielectric properties of the 95MCT ceramics by adding various additives or varying the preparation method [6, 7]. In our work, $ZnNb_2O_6$ was chosen as a sintering aid to lower the sintering temperature of 95MCT ceramics due to its excellent microwave dielectric properties and sintering temperature as low as 1150 °C [8]. The microstructure and the microwave dielectric properties of $ZnNb_2O_6$-doped 95MCT ceramics were investigated.

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Experimental procedures

High-purity reagents, $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$, TiO_2, $CaCO_3$, Nb_2O_5, and ZnO, were used as the starting materials, which were mixed and grounded in a balling mill with distilled water for 20 h according to the stoichiometry $MgTiO_3$, $ZnNb_2O_6$ and $CaCO_3$ powders, designated as A, B and C, respectively. Mixtures A were dried and calcined at 850, 900 and 950°C respectively, followed by XRD identification. Mixtures B and C were dried and calcined at 1000 °C and 1150 °C, respectively. The calcined regents were then mixed according to the desired composition 95MCT + x wt% $ZnNb_2O_6$ (x = 3, 4, 5, 6, 7, 8) and grounded into fine powder for 20 h. The fine powder together with the organic binder were forced through a 50-mesh sieve and pressed into pellets with dimensions of 18 mm in diameter and 8 mm in thickness. After debinding, these pellets were sintered at different temperatures.

The densities of the sintered ceramics were measured using the Archimedes method. Phase identification was carried out by using an X-ray diffractometer (Philips X'Pert Pro MPD) with CuK_α radiation and X'Pert software. The microstructure was observed using a scanning electron microscope (SEM). The dielectric constant and the unloaded Q values were measured by employing the Hakki–Coleman dielectric resonator method [9]. The apparatus consists of parallel conducting brass plates and coaxial probes connected to a HP83752A vector network analyzer and a HP sweep oscillator. The temperature coefficient of resonant frequency was obtained by measuring $TE_{01\delta}$ resonant frequency at 25 °C and 100 °C, respectively, and then calculated by the equation as follows, applied to the following equation:

$$\tau_f = \frac{f_{100} - f_{25}}{75 \times f_{25}} \times 10^6 (\mathrm{ppm}/^\circ\mathrm{C})$$

Results and discussion

Figure 1 shows the X-ray diffraction patterns of composition A calcined at different temperatures. On the basis of XRD results, it is confirmed that a, b and c are all composed of phase pure $MgTiO_3$ and a second phase of Mg_2TiO_5 did not occur as some researches reported. It is presumed that the adoption of high pure $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ results in the disappearance of the second phase. The decomposition reaction of magnesium carbonate basic pentahydrate during heat processing can be written as follows [10]:

$$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O \xrightarrow{258^\circ C} 4MgCO_3 + Mg(OH)_2 + 5H_2O(g)$$

$$Mg(OH)_2 \xrightarrow{405^\circ C} MgO + H_2O(g)$$

$$MgCO_3 \xrightarrow{543^\circ C} MgO + CO_2(g)$$

The fresh MgO with grain size in nano-scale and a high cm^2/g ratio produced by the decomposition of magnesium carbonate basic pentahydrate has high reactivity, which can react with TiO_2 easily. The accelerated reaction not only prompts the formation of pure phase of $MgTiO_3$, but also lowers its calcined temperature. At the beginning of the formation of fresh MgO, due to the insufficiency of fresh MgO and excess of TiO_2, the reaction can be described as follows:

$$MgO + TiO_2 \rightarrow MgTiO_3 \qquad MgO + 2TiO_2 \rightarrow MgTi_2O_5$$

With the decomposition of magnesium carbonate basic pentahydrate, the fresh Mgo becomes to be excess and then, the following reactions happen:

$$MgO + TiO_2 \rightarrow MgTiO_3 \qquad MgTi_2O_5 + MgO \rightarrow 2MgTiO_3$$

According to the XRD patterns (Fig. 1), the chemical reaction finished at a temperature lower than 850 °C. With the elimination of contaminant phase $MgTi_2O_5$, the resultant is pure $MgTiO_3$. Moreover, some reactions, which should occur during sintering, finished during the

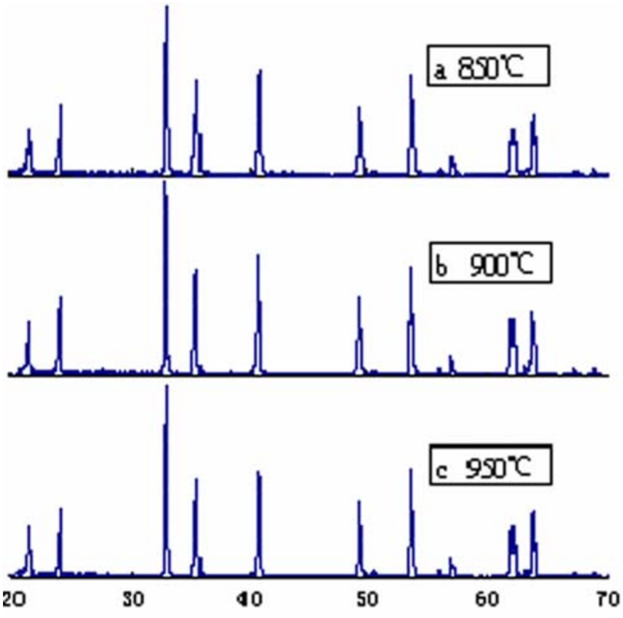

Fig. 1 XRD patterns of $MgTiO_3$ powders calcined at different temperatures: (**a**) 850 °C; (**b**) 900 °C; (**c**) 950 °C

calcination process with the evaporation of gases such as H_2O and CO_2, which can reduce the volume shrinkage and pores ratio of the ceramic sample during sintering. As a result, the ceramic is more compact and the dielectric performance is improved.

The XRD patterns of 95MCT + x wt.%$ZnNb_2O_6$ (x = 3, 5, 7) are shown in Fig. 2. The XRD analysis proves that no evidence of $ZnNb_2O_6$ phase and the diffraction peaks belong only to $MgTiO_3$ phase. The result can be explained as: $ZnNb_2O_6$ mainly exists in the grain boundaries of $MgTiO_3$ in the form of glass because the sintering temperature of $ZnNb_2O_6$ is very low and $ZnNb_2O_6$ is melted during sintering. On the other hand, $ZnNb_2O_6$ has a different crystal structure from the $MgTiO_3$ so that it is difficult for $ZnNb_2O_6$ to form solid solution with $MgTiO_3$. Thus, there is no $ZnNb_2O_6$ phase observed in the XRD patterns.

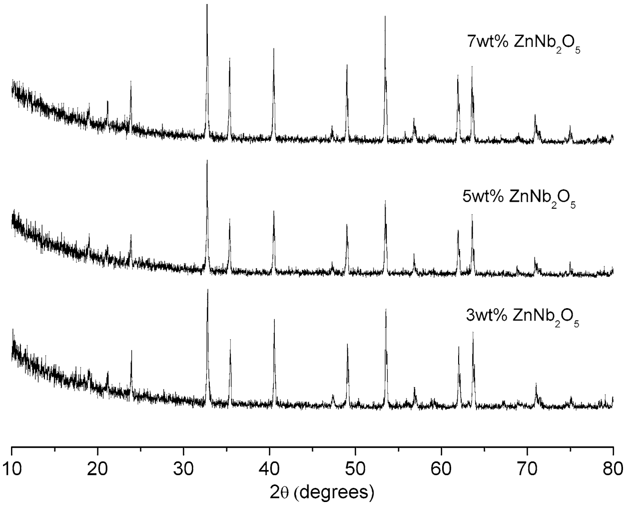

Fig. 2 XRD pattern of 6 wt.% $ZnNb_2O_6$doped 95MCT ceramic sintered at 1300 °C

SEM photographs of 95MCT ceramics with various $ZnNb_2O_6$ amounts and sintered at different temperatures are illustrated in Fig. 3. The 95MCT ceramic, which was doped with 5 wt.% $ZnNb_2O_6$ and sintered at 1300 °C, were full of pores and the shape of grains was not uniform (Fig. 3a). As the amount of $ZnNb_2O_6$ increased to 6 wt.%, the grain growth increased rapidly and pores were almost eliminated (Fig. 3b). The liquid phase sintering effect was clearly observed in the grain morphology doping with 6 wt.% $ZnNb_2O_6$. The composition with 6 wt.% $ZnNb_2O_6$ exhibited more uniform grain size than the sample with 5 wt.% addition, due to more liquid phase wetting the grains of 95MCT ceramics. However, inhomogeneous grain growth was observed as the amount of $ZnNb_2O_6$ increased to 7 wt% (Fig. 3c). It was presumed that the amount of liquid phase was too much and spread to the ceramic surface. Moreover, the liquid phase congregated and formed monstrous grains due to surface tension. On the other hand, the liquid phase could not be distributed over the grain boundaries equably as the result of over high sintering temperatures. Thus, the grain size of 95MCT ceramics with 7 wt.% $ZnNb_2O_6$ was smaller than that of the ceramics with 6 wt.% $ZnNb_2O_6$. As shown in Fig. 3d, the sample doped with 6 wt.% $ZnNb_2O_6$ and sintered at

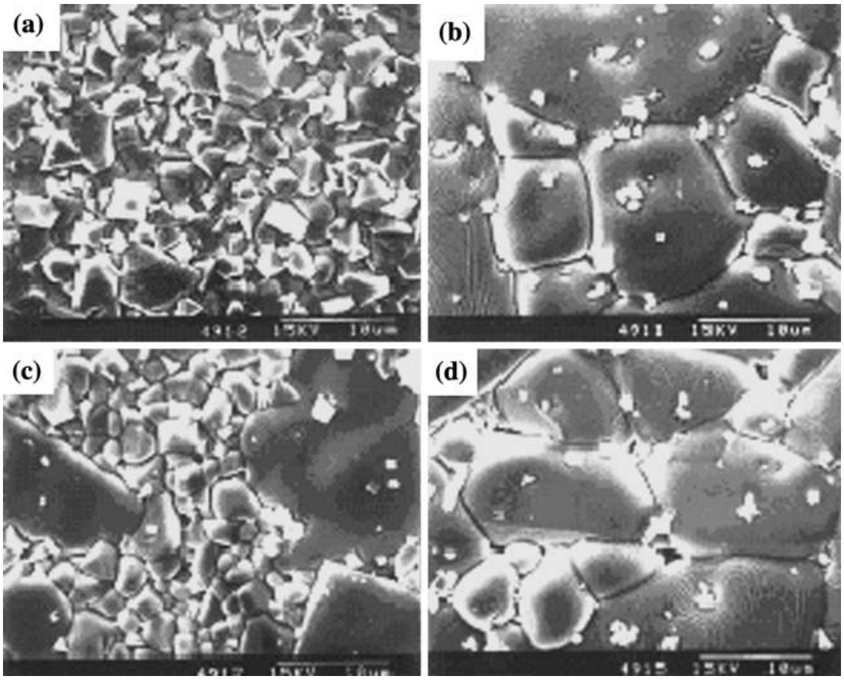

Fig. 3 SEM photographs of 95MCT + x wt.% $ZnNb_2O_6$ ceramics (**a**) 5 wt.%, sintered at 1300 °C; (**b**) 6 wt.%, sintered at 1300 °C; (**c**) 7 wt.%, sintered at 1300 °C; (**d**) 6 wt.%, sintered at 1260 °C

1260 °C, was full of pores, which illuminated that the sintering temperature need to be increased.

Figure 4 shows the correlations between the dielectric constant of 95MCT + x wt.% $ZnNb_2O_6$ (x = 3, 4, 5, 6, 7, 8) ceramics with content when sintered at 1280 °C and 1300 °C, respectively. The dielectric constant slightly increases with increasing the amount of $ZnNb_2O_6$ on the conditions of two sintering temperatures, because the dielectric constant of 95MCT is smaller than that of $ZnNb_2O_6$. The dielectric constant obeys the well-known mixing rule as below [11].

$$\ln\varepsilon_r = v_1\ln\varepsilon_1 + v_2\ln\varepsilon_2 + v_3\ln\varepsilon_3$$

Where, v_1, v_2 and v_3 denote the volume fraction of $MgTiO_3$, $CaTiO_3$ and $ZnNb_2O_6$, respectively.

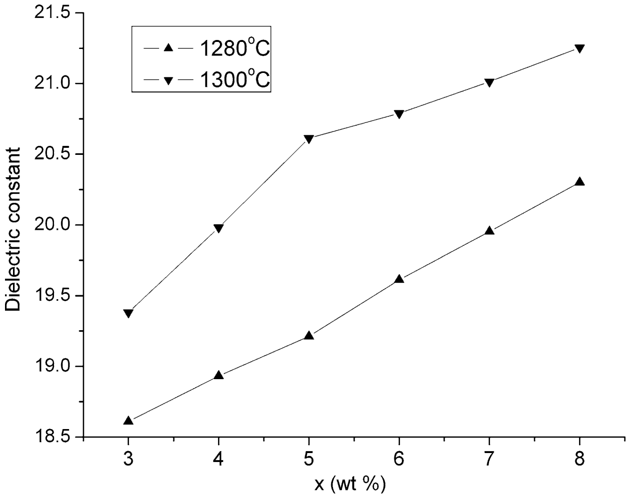

Fig. 4 Dependence of dielectric constant of 95MCT + x wt.% $ZnNb_2O_6$ (x = 3, 4, 5, 6, 7, 8) ceramics on the $ZnNb_2O_6$ content

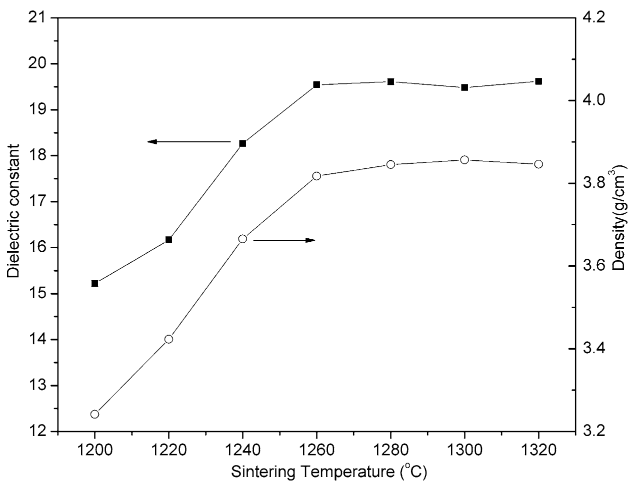

Fig. 5 Dependences of dielectric constant and density on the sintering temperatures of 6 wt.% $ZnNb_2O_6$ doped 95MCT ceramics

Figure 5 depicts the dependences of dielectric constant and density on the sintering temperatures of 6 wt.% $ZnNb_2O_6$ doped 95MCT ceramics. At a sintering temperature of 1200 °C, the ceramic cannot be well sintered. Thus, the low dielectric constant is due to the low density. As the temperature increases, the density increases apparently, so does the dielectric constant. Above 1280 °C, the ceramics can be sintered with high density. Accordingly, the density and dielectric constant of the ceramics are almost unchanged.

As shown in Fig. 6, the quality factor of 95MCT + x wt.%$ZnNb_2O_6$ (x = 3, 4, 5, 6, 7, 8) ceramics increases to maximum and thereafter decreases with an increase of $ZnNb_2O_6$ amount. The increase of quality factor is

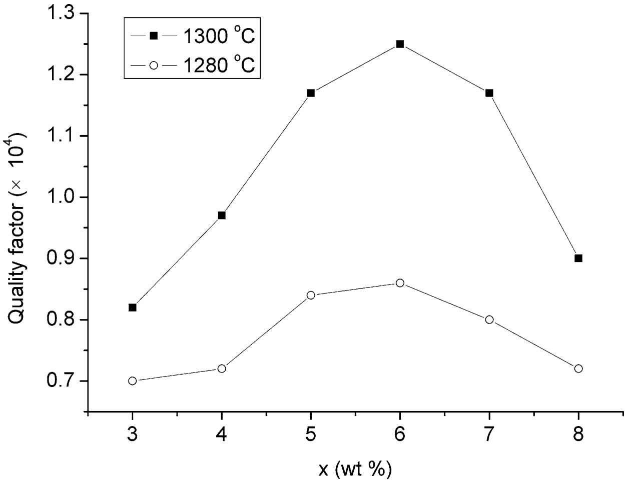

Fig. 6 The quality factor of 95MCT + x wt.% $ZnNb_2O_6$ (x = 3, 4, 5, 6, 7, 8) ceramic

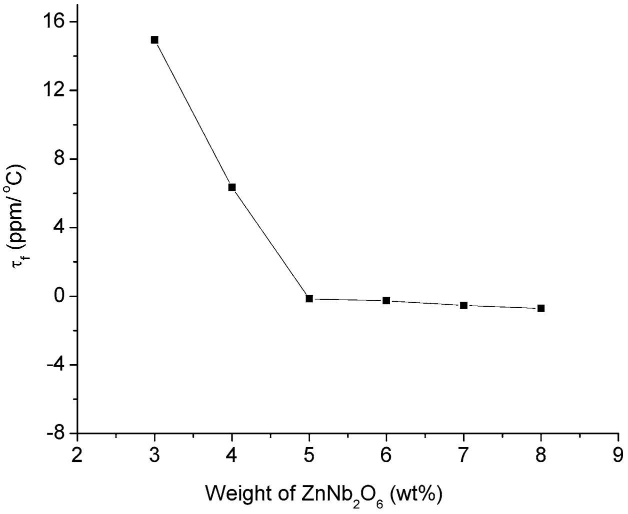

Fig. 7 The temperature coefficient of resonant frequency for 6 wt.% $ZnNb_2O_6$ doped 95MCT ceramic sintered at 1300 °C

attributed to the reduction of pores and the grain growth. On the other hand, the degradation of quality factor with high $ZnNb_2O_6$ content is due to inhomogeneous grain growth, resulting in a reduction of density as observed in Fig. 3. According to previous reports, the quality factor is simultaneously affected by many factors, mainly caused not only by the lattice vibration modes, but also by densification, pores, grain size, grain boundaries and second phases [12]. As the sintering temperature increases, it is found that the quality factor increases too.

Other researchers have reported a zero τ_f value of 95MCT ceramic. However, in our experiments, the 95MCT ceramics doesn't have a zero τ_f. It may be attributed to the raw materials and the process condition that is different from the previous report. As shown in Fig. 7, the τ_f values are dependent on different $ZnNb_2O_6$ contents. When the weight percentage of $ZnNb_2O_6$ is low, the τ_f is positive. Then the τ_f values decrease with $ZnNb_2O_6$ content increasing and τ_f is close to zero with about 5 wt% $ZnNb_2O_6$. It is interesting to find that the τ_f values maintain zero when the weight percentage of $ZnNb_2O_6$ is above 5 wt%. This phenomenon can be explained as: the excess $ZnNb_2O_6$ exists in the grain boundary in the form of glass, which is proved by XRD in Fig. 1. Thus, the excess $ZnNb_2O_6$ contributes little to the τ_f.

Conclusions

$(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ and TiO_2 mixed according to the stoichiometry of $MgTiO_3$ can synthesize phase pure $MgTiO_3$. MgO introduced by $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$ has a high reactivity and accelerates the formation of $MgTiO_3$. With 6 wt.% $ZnNb_2O_6$ addition, the sintering temperature of 95MCT can be lowered to 1300 °C. Simultaneously, it process excellent microwave dielectric properties: ε_r: 21, Q × f: 130,000 (at 13 GHz) and a zero τ_f value.

References

1. Sohn J-H, Inaguma Yoshiyuki et al (1994) Jpn J Appl Phys 33:5466
2. Sreedhar K, Pavaskar NR (2002) Mater Lett 53:452
3. Abothu IR, Prasada Rao AV, Komarneni S (1999) Mater Lett 38:186
4. Cheng H, Xu B, Ma J (1997) J Mater Sci Lett 16:1570
5. Huang C-L, Pan C-L, Shium S-J (2002) Mater Chem Phys 78:111
6. Huang C-L, Weng M-H (2001) Mater Res Bull 36:2741
7. Huang C-L, Pan C-L (2002) Jpn J Appl Phys 41:707
8. Lee HJ, Kim IT, Hong KS (1997) Jpn J Appl Phys 36:1318
9. Hakki BW, Coleman PD (1960) IEEE Trans Microwave Theor Tech 8:402
10. Wu S-H, Wu G-Q (1999) Bull Chinese Ceram Soc 6:3
11. Werisng W (1991) In: Steele BCH (ed) Electronic ceramic. Elsevier Applied Science, London, p 67
12. Kim WS, Hong HT, Kim ES et al (1998) Jpn J Appl Phys 37:5367