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Low-temperature synthesis and microwave dielectric properties of trirutile-structure $MgTa_2O_6$ ceramics by aqueous sol–gel process

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Abstract

Trirutile-structure $MgTa_2O_6$ ceramics were prepared by aqueous sol–gel method and microwave dielectric properties were investigated. Highly reactive nanosized $MgTa_2O_6$ powders were successfully synthesized at 500 °C in oxygen atmosphere with particle sizes of 20–40 nm. The evolution of phase formation was detected by DTA–TG and XRD. Sintering characteristic and microwave dielectric properties of $MgTa_2O_6$ ceramics were studied at different temperatures ranging from 1100 to 1300 °C. With the increase of sintering temperature, density, ε_r and $Q \cdot f$ values increased and saturated at 1200 °C with excellent microwave properties of $\varepsilon_r \sim 30.1$, $Q \cdot f \sim 57{,}300$ GHz and $\tau_f \sim 29$ ppm/°C. The sintering temperature of $MgTa_2O_6$ ceramics was significantly reduced by aqueous sol–gel process compared to conventional solid-state method.

Keywords: A. Sol–gel process; $MgTa_2O_6$; Nanopowder synthesis; Microwave dielectric properties

1. Introduction

The rapid progress in mobile and satellite communication system were creating high demands for the development of microwave dielectric materials with a high quality factor, an appropriate dielectric constant, and a near-zero temperature coefficient of resonant frequency. High quality AB_2O_6 (A = Ca, Mg, Mn, Co, Ni, Zn and B = Nb, Ta) compounds were investigated as microwave dielectric resonators by Lee et al. [1]. Lee et al. reported that $MgTa_2O_6$ (MT) sintered at 1550 °C exhibited relative dielectric constant (ε_r) of 30.3, quality factor ($Q \cdot f$) of 59,600 GHz, and temperature coefficient of resonant frequency (τ_f) of 30 ppm/°C by solid state process. Obviously high sintering temperatures would limit their applications for practical cases, so the reduction of sintering temperatures was desirable to enable commercial applications such as in integrated circuits. Usually it was believed that lowering sintering temperature could be achieved by many methods such as adding glass flux and using starting materials with smaller particle sizes. As we known, adding glass flux usually caused detrimental effect on microwave properties of ceramics. The synthesis of MT powders was widely investigated [2–4] and now in order to reduce sintering temperature and improve sintering ability there were many other investigations of chemical processing or special methods [5,6], which were developed as alternatives to the conventional solid-state reaction of mixed oxides for producing ceramics using starting materials with smaller particle sizes. Among these wet chemical techniques, the sol–gel was undoubtedly one of useful process for producing powders with good control over stoichiometry and homogeneity, yielding nano-sized particles and widely used in many other ceramics system [7–10]. However, few researches about microwave properties of MT ceramics fabricated by aqueous sol–gel process were reported in the present literatures.

In this paper the sol–gel method was used to synthesize nano-sized powders as precursors for preparation of MT ceramics instead of other methods. The whole process involved all complexation of aqueous metal ions by non-toxic poly functional carboxyl and avoided complex steps such as refluxing of alkoxides, resulting in less time consumption compared to other techniques. The evolution of MT phase

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formation and microwave dielectric properties of MT ceramics as a function of sintering temperatures were investigated in detail. Experimental results showed that the preparation of MT ceramics with retaining excellent microwave properties could be obtained efficiently and simply at low sintering temperatures by aqueous sol–gel process.

2. Experimental

Analytical-grade Ta_2O_5, K_2CO_3, $Mg(NO_3)\cdot 6H_2O$, HNO_3, citric acid (CA) and ethylene glycol (EG) were used as raw materials to synthesize MT nanopowders as shown in Fig. 1. Firstly, the mixture of Ta_2O_5 and K_2CO_3 was co-melted at 900 °C in order to obtain K_3TaO_4 compounds according to phase diagrams. Subsequently, K_3TaO_4 compounds were dissolved in distilled water, then pH value was controlled at ~2 to ensure the formation of $Ta(OH)_5$ precipitate. The whole formation process of $Ta(OH)_5$ phases could be formulated from Eqs. (1)–(4). Thirdly, $Ta(OH)_5$ precipitate was filtered off and washed with distilled water for six times to remove K^+ ions and then dissolved completely in citric acid water solution by continuous magnetic stirring at 300 rpm for 15 min. Meanwhile, a stoichiometric amount of $Mg(NO_3)\cdot 6H_2O$ was added to above solution and then the solution was stirred for another 30 min. Finally, ethyl alcohol (20–40 ml) was added to the as-prepared mixed solution in drops and stirred for 1 h to form a transparent and stable sol. pH of the solution was maintained in the range of 3.5–5 by adding buffering agents. The sol was heated at 80–90 °C for 1 h to obtain a xerogel. The xerogel was decomposed at 500 °C using a muffle furnace for crystallization in oxygen atmosphere. The as-prepared powers were ball milled in a polyethylene jar for 4 h using ZrO_2 balls in ethanol medium to reduce conglobation phenomena. Powders were then mixed with polyvinyl alcohol as a binder, granulated and pressed into cylindrical disks of 10 mm diameter and about 5 mm height at a pressure of about 200 MPa. These pellets were preheated at 600 °C for 4 h to expel the binder and then sintered at selected temperatures for 2 h in air at a heating rate of 5 °C/min.

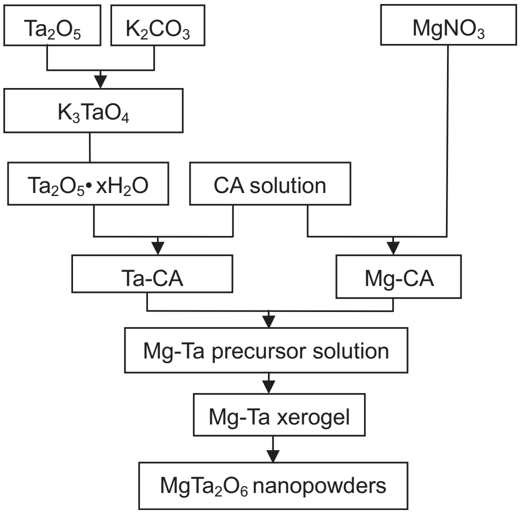

Fig. 1. Chart for the synthesis of MT nanopowders by aqueous sol–gel processing.

$$3K_2CO_3 + Ta_2O_5 \rightarrow 5K_3TaO_4 + CO_2. \quad (1)$$

$$6K_3TaO_4 + 5H_2O \rightarrow 18K^+ + Ta_6O_{19}^{8-} + 10OH^-. \quad (2)$$

$$4K^+ + Ta_6O_{19}^{8-} + 4OH^- + 8H^+ \rightarrow K_4H_4Ta_6O_{19}\downarrow + 4H_2O. \quad (3)$$

$$K_4H_4Ta_6O_{19} + 15H^+ + 11OH^- \rightarrow 6Ta(OH)_5\downarrow + 4K^+. \quad (4)$$

In order to analyze the evolution of MT phase formation, the as-formed MT xerogel was characterized using thermogravimetry (TG) and differential thermal analysis (DTA) to study its thermal properties. Phase analysis of MT powders was conducted with the help of a Rigaku diffractometer (Model D/MAX-B, Rigaku Co., Japan) using Ni filtered Cu Kα radiation (λ = 0.1542 nm) at 40 kV and 40 mA settings. Based on XRD analysis, raw MT powders were examined for their morphology and particle size using a transmission electron microscopy (Model JEOL JEM-2010, FEI Co., Japan). Bulk densities of sintered ceramics were measured by the Archimedes method. An HP8720ES network analyzer (Hewlett-Packard, Santa Rosa, CA) was used for the measurement of microwave dielectric properties. Dielectric constants were measured using Hakki-Coleman post-resonator method by exciting the TE011 resonant mode of dielectric resonator using an electric probe as suggested by Hakki and Coleman and Courtney [11]. Unloaded quality factors were measured using TE01d mode by the cavity method [12]. All measurements were made at room temperature and in the frequency of 8–10 GHz. Temperature coefficients of resonant frequency were measured in the temperature range of 25–85 °C.

3. Results and discussion

Fig. 2 showed TG–DTA curves of MT xerogel in pure oxygen atmosphere at a heating rate of 10 °C/min. The results indicated that obvious weight losses began at 250 °C and all chemical reactions involving weight losses, such as decom-

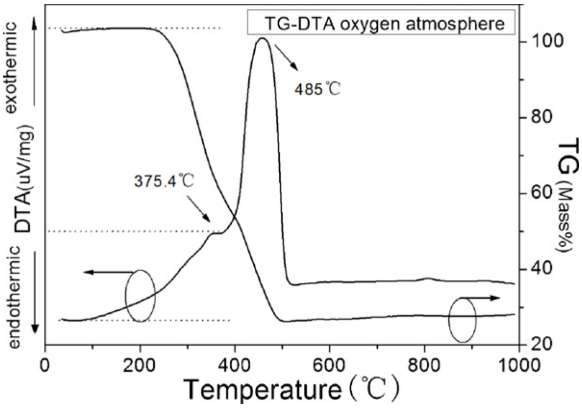

Fig. 2. TG–DTA curves of MT xerogel in oxygen atmosphere.

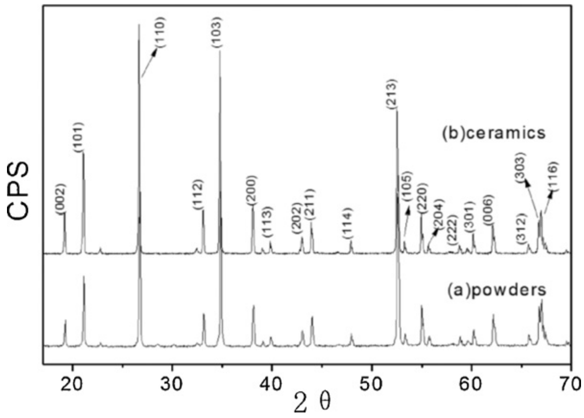

Fig. 3. X-ray diffraction patterns of MT xerogel calcined at (a) 500 °C for 30 min and ceramics sintered at 1200 °C for2 h.

position of organic polymeric network, finished completely below 500 °C. Total weight loss was about 80%, which occurred in two steps: (i) initial weight loss (about 40%) below 400 °C, resulting from the evaporation of residual solvent and decomposition of organic polymeric network with evolution of CO_2 and H_2O, with endothermic peaks ranging from 250 to 400 °C, and (ii) second weight loss (about 20–30%) in TG curves, combined with an significantly exothermal peak in the temperature region of 400–500 °C, which was attributed to the oxidation of metal–organic groups. TG results of MT xerogel were also similar with the report by the sol–gel method [5]. No further significant weight loss and thermometric peaks were observed above 500 °C in TG–DTA curves, indicating the minimum firing temperature to synthesize magnesium niobate phase.

The XRD pattern of MT xerogel calcined at 500 °C for 30 min in oxygen atmosphere were shown in Fig. 3(a). It was pleasantly found that the crystallization of MT phase took place obviously at 500 °C, this phenomenon was recognized from exothermic peaks of DTA and corresponding TG profile as described above. The xerogel fired at 500 °C consisted of predominant peaks of $MgTa_2O_6$ matching with JCPDS file number 32-0321, also free from any second phases such as $Mg_5Ta_4O_{15}$ or $Mg_4Ta_2O_9$. All reflections in diffraction pattern could be indexed on the basis of an orthorhombic phase with refined lattice parameters (as obtained by a least squares fit to observed d values) of $a = b = 4.718$ Å and $c = 9.204$ Å. In Fig. 3(a) the influence of calcination temperature on X-ray diffraction of powders was observed in variations of intensity and full width at half maximum (FWHM), characteristic peaks of (1 0 3) and (1 1 0) were narrower and stronger, which was associated with the crystallization of powders. According to the Scherer formula ($D = K\lambda/\beta \cos \theta$) [13], particle sizes of MT powders at 500 °C were calculated to be 28 nm. XRD results indicated that calcination temperature of synthesizing pure MT phase was remarkably decreased to 500 °C by aqueous sol–gel method, which showed obvious advantages in comparison to these of conventional mixed oxide routes reported before [3,4] and other chemical methods [2,5,6] as shown in Table 1. To be contrast, as-prepared MT ceramics sintered at temperatures ranging 1100–1300 °C also showed similar XRD patterns just

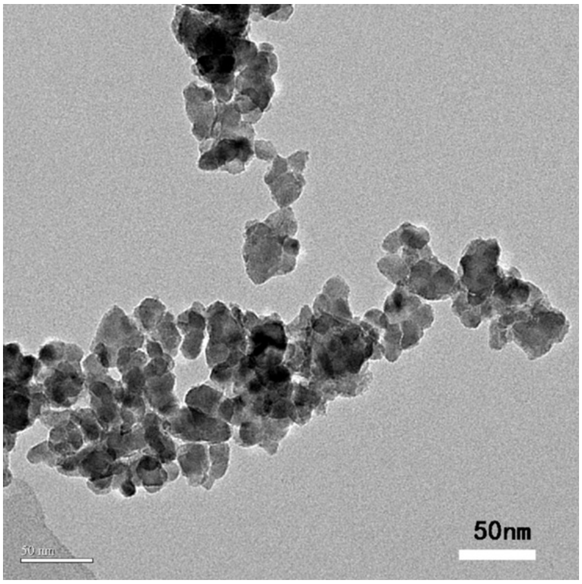

Fig. 4. TEM micrograph of raw MT nanopowders calcined at 500 °C for 30 min.

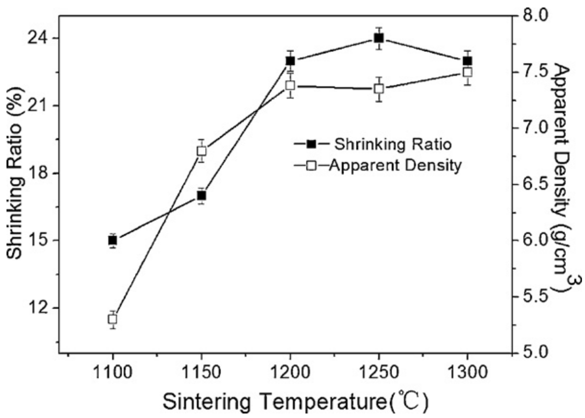

Fig. 5. Apparent densities and Shrinkaging ratio of MT ceramics as a function of sintering temperatures.

Table 1
Comparison of $MgTa_2O_6$ powders synthesized by different methods.

Process	Calcination temperature (°C)	Grain size (nm)	References
Molten salt method	850	500–1000	[2]
Conventional solid state method	900/1250	∼1000/∼830	[3,4]
Citrate sol–gel method	900	25–100	[5]
Co-precipitation method	550	40	[6]
Aqueous sol–gel	500	20–40	Our results

with sharper peaks as shown in Fig. 3(b), which indicated that $MgTa_2O_6$ phase existed as predominant phase in a status of excellent crystallization.

TEM micrograph of MT nanopowders calcined at 500 °C was illustrated in Fig. 4. As observed in the image, it was worth noting that particles were slightly agglomerated due to high surface to volume ratio and basically regular in shape. Particle sizes were measured by the liner intercept method [14] with the range of about 20–40 nm and the range of particle size was in good coincidence with the calculated results of Scherer formula mentioned above. For comparison, MT particle sizes synthesized by different methods were also listed in Table 1 and the results showed that MT powders had smaller particle size of 20–40 nm by aqueous sol–gel process with larger surface area and free energy. Since the surface free energy is considered to be a driving force in the sintering process, a number of sintering models have been researched for initial sintering stage and the resulting equation has been deduced. According to sintering equation of initial stage [15], the use of MT nanopowders as starting materials was effective in preparing high density MT ceramics promisingly through low-temperature sintering and short sintering time. Therefore, the sol–gel process showed significant advantages of sintering ceramics at low temperatures, which were demonstrated by many other reports.

Sintering characteristics of samples depending on sintering temperatures were plotted in Fig. 5. Fig. 5 represented curves of

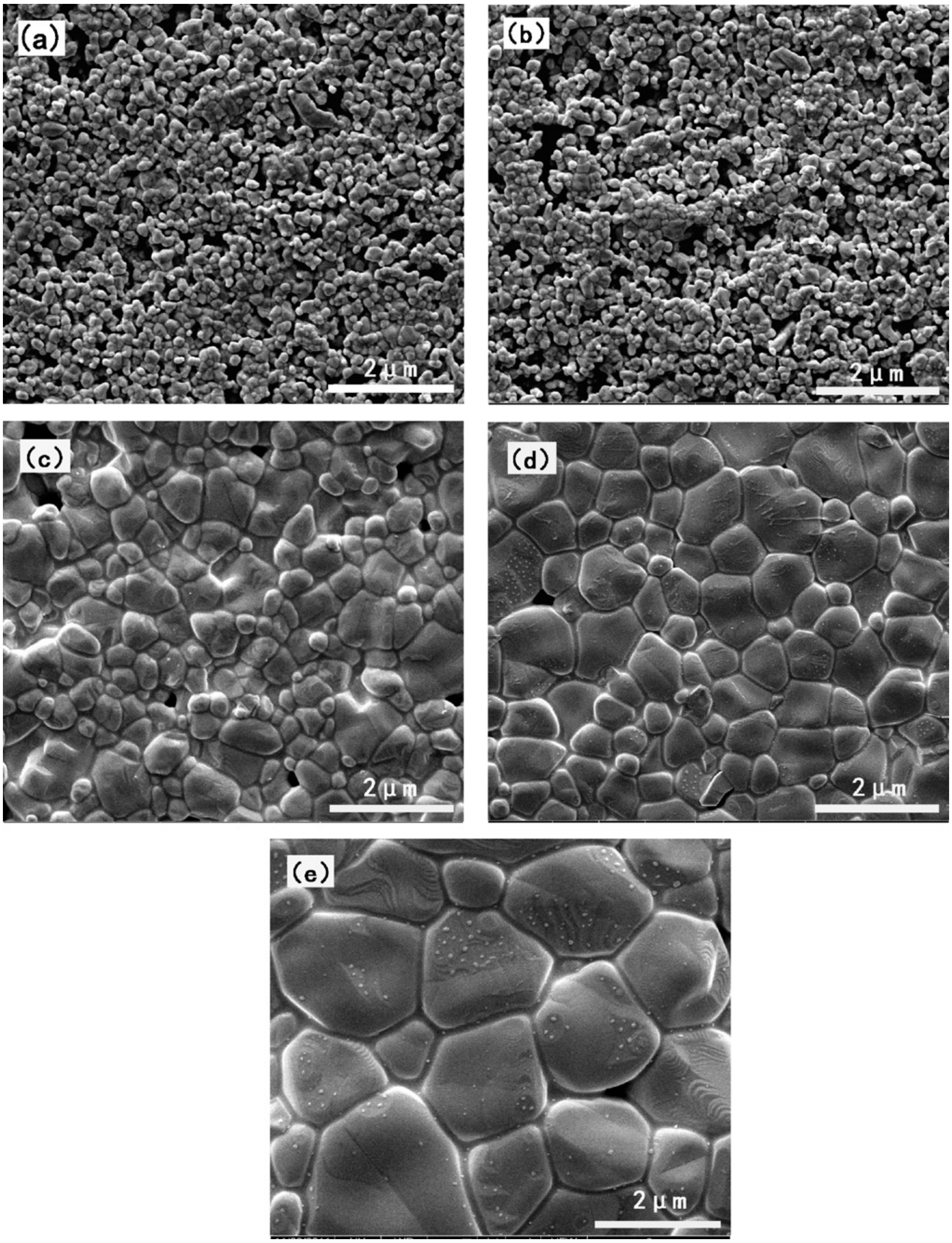

Fig. 6. FE-SEM micrographs of MT ceramics sintered at different sintering temperatures for 2 h ((a)–(f) corresponding to 1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C).

apparent densities and diametric shrinkage ratio of MT ceramics as a function of sintering temperature, through which the optimized sintering temperature was determined. Apparent densities increased from 5.3 to 7.5 g/cm^3 as sintering temperatures increased from 1100 to 1300 °C. A saturated value of apparent densities was obtained at 1200 °C. The curve of diametric shrinkage ratio showed the similar tendency and also increased with an increase of sintering temperatures, and then saturated at about 1200 °C. SEM micrographs of MT ceramics sintered at different temperatures for 2 h were illustrated in Fig. 6(a–e). Changes in porosity and grain size could be seen with an increase of sintering temperature. Apparent porosity decreased as sintering temperature increased from 1100 to 1200 °C and all pores almost disappeared at 1200 °C on the surface of MT samples. As sintering temperature increased, grain size increased rapidly and average grain size measured by a linear intercept method [14] was about ~1 μm at 1200 °C as shown in Fig. 6(c). It was shown that MT ceramics were successfully prepared with high density through sol–gel process at 1200 °C and sintering temperature was reduced significantly compared to solid-state reaction methods [16–18].

Plots of ε_r, $Q \cdot f$ and τ_f values were shown in Fig. 7 as a function of sintering temperatures. ε_r values of MT ceramics steadily increased from 16.3 to 29.7 as sintering temperatures ranged from 1100 to 1200 °C, and then saturated at ~30. Based on results of sintering characteristic and microstructure as shown in Fig. 6, it was obvious that low ε_r values were caused by undense microstructure of MT ceramics with much pores at sintering temperatures <1200 °C. ε_r values were approximately saturated about 30 at sintering temperatures >1200 °C. The curve of ε_r values showed a similar tendency with those of apparent density and shrinkage ratio, which were sensitive to dense degree of ceramics significantly. In general, higher density could achieve higher dielectric constant owing to a lower amount of pores ($\varepsilon_r \sim 1$). The results of ε_r values obtained at 1200 °C by sol–gel process were comparable with these results sintered at 1400 °C by solid-state reaction methods [16–18]. In addition, to clarify effects of crystal structure on dielectric constant, theoretical dielectric polarizability ($\alpha_{\text{theo.}}$) was calculated to be ~23.06 by additive rule with ionic polarizability of composing ions or oxides [19] as formulated in Eq. (5) and observed dielectric polarizability ($\alpha_{\text{obs.}}$) was calculated to be 22.16 by Clauses–Mosotti equation as formulated in Eq. (6) with measured dielectric constant at microwave frequencies [20]. Values of $\alpha_{\text{theo.}}$ and $\alpha_{\text{obs.}}$ were in good agreement with each other and the minor deviation from the $\alpha_{\text{obs.}}$ and $\alpha_{\text{theo.}}$ could attribute to relative density because the $\alpha_{\text{obs.}}$ value depended on specimens and fabrication process.

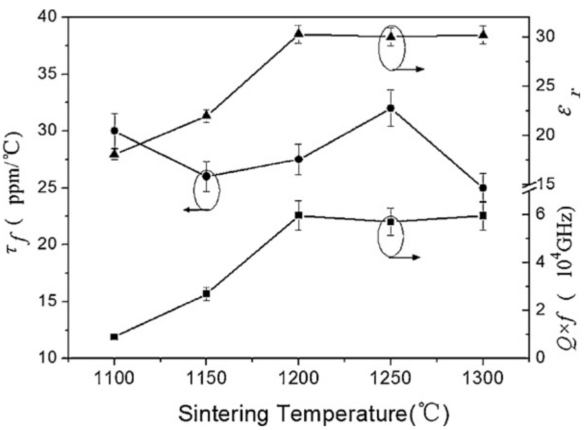

Fig. 7. Curves of ε_r, $Q \cdot f$ and τ_f values as a function of sintering temperatures for MT ceramics in the temperature region of 1100–1300 °C.

$$\alpha_{\text{theo.}} = \alpha(\mathrm{MgTa_2O_6}) = \alpha(\mathrm{MgO}) + \alpha(\mathrm{Ta_2O_5}) \tag{5}$$

$$\alpha_{\text{obs.}} = \frac{1}{b}\left[\frac{Vm(\varepsilon - 1)}{\varepsilon + 1}\right] \tag{6}$$

where α (MgO) and α (Ta_2O_5) represented oxides polarizabilities reported by Shannon [19]. Moreover, Vm, ε and b indicated the molar volume of samples, dielectric constant and constant value ($4\pi/3$), respectively.

With increasing sintering temperatures from 1100 to 1200 °C, $Q \cdot f$ values increased from 15,365 to 57,300 GHz with saturated $Q \cdot f$ values ~57,300 GHz in the sintering temperature region of 1200–1300 °C. The remarkable increase in $Q \cdot f$ values ranging from 1100 to 1200 °C was also related to the reduction of porosity according to results of SEM microstructures as shown in Fig. 6(a–c). As for $Q \cdot f$ values of dielectric ceramics, it was known that porosity, secondary phase, structure defect and grain boundary of ceramics produced a deterioration in $Q \cdot f$ values as extrinsic factors [21]. Among these factors, associated with our results the porosity was suggested to affect $Q \cdot f$ values obviously at sintering temperatures less than 1200 °C. Relative density was one of important factor in controlling dielectric loss, which was shown on many other microwave dielectric materials. Due to increased density $MgTa_2O_6$ ceramics sintered at 1200 °C had excellent $Q \cdot f$ value of 57,300 GHz, which was comparable with the result of $Q \cdot f \sim 59{,}600$ GHz while sintered at 1550 °C by the solid-state method [16–18]. While the as-prepared samples were of nearly full density, $Q \cdot f$ values were affected by intrinsic factors, such as crystal structure and lattice vibrations, especially covalence of cation-oxygen bonds. Thus, covalence of cation-oxygen bonds of compounds was also calculated using refined bond length and the relationship between covalence and bond length was further discussed in detail in next work. Moreover, remarkable variations in τ_f values of MT ceramics were not recognized with sintering temperatures from 1100 to 1300 °C and these values ranged from 25 to 35 ppm/°C. Thus, it was considered that additional improvement in τ_f value was required for dielectric resonator applications at high frequency.

4. Conclusions

Trirutile-structure $MgTa_2O_6$ powders with particle sizes of nearly 20–40 nm were obtained successfully by aqueous sol–gel synthetic route, which showed major advantages over other methods reported before. A considerable decrease in calcinations temperature (at 500 °C) was obtained in pure oxygen atmosphere for the formation of $MgTa_2O_6$ nanopowders. Moreover, the sintering ability and microwave properties of $MgTa_2O_6$ ceramics were systematically investigated at different sintering temperatures. $MgTa_2O_6$ samples with nearly full densities were obtained at 1200 °C and showed excellent microwave dielectric properties of $\varepsilon_r = 30.1$, $Q \cdot f = 57{,}300$ GHz and $\tau_f = 28$ ppm/°C.

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References

[1] H.J. Lee, I.T. Kim, K.S. Hong, Dielectric properties of AB_2O_6 compounds at microwave frequencies (A = Ca, Mg, Mn, Co, Ni, Zn, and B = Nb, Ta), Jpn. J. Appl. Phys. 36 (1997) L1318–L1320.

[2] A.K. Ganguli, S. Nangia, M. Thirumal, P.L. Gai, A new form of $MgTa_2O_6$ obtained by the molten salt method, J. Chem. Sci. 118 (2006) 37–42.

[3] M. Thirumal, A.K. Ganjuli, Synthesis and dielectric properties of magnesium niobate–magnesium tantalate solid solutions, Mater. Res. Bull. 36 (2001) 2421–2427.

[4] C.R. Ferrari, A.C. Hernandes, $MgTa_2O_6$ and $ZnTa_2O_6$ ceramics from oxide precursors, J. Eur. Ceram. Soc. 22 (2002) 2101–2105.

[5] Y.C. Zhang, B.J. Fu, Y.H. Liu, Y.H. Liu, X. Wang, T. Li, Z.X. Yue, Synthesis of $MgTa_2O_6$ nano-powders by citrate sol–gel method, J. Alloys Compd. 505 (2010) 750–753.

[6] S.C. Navale, V. Samuel, V. Ravi, Low temperature synthesis of $MgTa_2O_6$ powders, Mater. Lett. 59 (2005) 3926–3928.

[7] H. Zhu, Z.J. Guo, W.D. Yang, W.F. Chang, C.C. Wang, Preparation and characterization of nanometer-sized $(Pb_{1-x}Ba_x)TiO_3$ powders using acetylacetone as a chelating agent in a non-aqueous sol–gel process, Ceram. Int. 37 (2011) 3203–3209.

[8] N.L. Wang, X.Y. Zhang, Z.H. Bai, H.Y. Sun, Q.S. Liu, L.P. Lu, X.Y. Mi, X.C. Wang, Synthesis of nanocrystalline ytterbium-doped yttria by citrate-gel combustion method and fabrication of ceramic materials, Ceram. Int. 37 (2011) 3133–3138.

[9] M.J.N. Isfahani, P.N. Isfahani, K.L.D. Silva, A. Feldhoff, Structural and magnetic properties of $NiFe_{2-x}Bi_xO_4$ ($x = 0$, 0.1, 0.15) nanoparticles prepared via sol–gel method, Ceram. Int. 37 (2011) 1905–1909.

[10] M.H. Ardakani, F. Moztarzadeh, M. Rabiee, A.R. Talebi, Synthesis and characterization of nanocrystalline merwinite ($Ca_3Mg(SiO_4)_2$) via sol–gel method, Ceram. Int. 37 (2011) 175–180.

[11] B.W. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IEEE Trans. 8 (1960) 402–410.

[12] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators, IEEE Trans. 18 (1970) 476–485.

[13] Y.K. Lakshmi, P.V. Reddy, Influence of sintering temperature and oxygen stoichiometry on electrical transport properties of $La_{0.67}Na_{0.33}MnO_3$ manganite, J. Alloys Compd. 470 (2009) 67–74.

[14] A. Thorvaldsen, The intercept method-2. Determination of spatial grain size, Acta Mater. 45 (1997) 595–600.

[15] S.-J.L. Kang, Sintering: Densification, Grain Growth & Microstructure, Elsevier Butterworth-Heinemann, Burlington, 2005.

[16] W.C. Tzou, Y.C. Chen, C.F. Yang, C.M. Cheng, Microwave dielectric characteristics of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics, Mater. Res. Bull. 41 (2006) 1357–1363.

[17] C.L. Huang, K.H. Chiang, C.Y. Huang, Microwave dielectric properties and microstructures of $MgTa_2O_6$ ceramics with CuO addition, Mater. Chem. Phys. 90 (2005) 373–377.

[18] C.F. Yang, C.C. Chan, C.M. Cheng, Y.C. Chen, The sintering and microwave dielectric characteristics of $MgTa_{1.5}Nb_{0.5}O_6$ ceramics, J. Eur. Ceram. Soc. 25 (2005) 2849–2852.

[19] R.D. Shannon, G.R. Rossman, Dielectric constants of silicate garnets and the oxide additivity rule, Am. Miner. 77 (1992) 94–100.

[20] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1993) 348–366.

[21] S.J. Penn, M.N. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, K. Schrapel, Effect of porosity and grain size on the microwave dielectric properties of sintered alumina, J. Am. Ceram. Soc. 80 (1997) 1885–1888.