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Lowering of sintering temperature and microwave dielectric properties of $BaTi_4O_9$ ceramics prepared by the polymeric precursor method

M.H. Weng*, T.J. Liang, C.L. Huang

Department of Electrical Engineering, National Cheng-Kung University, No. 1 University Road. Tainan, Taiwan, ROC

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Abstract

Low temperature sintering and microwave dielectric properties of barium polytitanate ($BaO–4TiO_2$) ceramics prepared by means of polymeric precursor route based on the Pechini process were investigated. Pure and fine $BaTi_4O_9$ powders with particle sizes of 100–200 nm were derived by thermal decomposition of amorphous gel precursor (above 750 °C). They formed single orthorhombic $BaTi_4O_9$ phase and showed fine and well-dispersed by XRD and SEM observation. The high sintering ability of the prepared powders enabled the fabrication of dielectric ceramics at low sintering temperatures (1200–1300 °C). The well-sintered $BaTi_4O_9$ ceramics with high relative densities (95%) were found to show excellent microwave dielectric properties compared to those prepared by conventional method at the same sintering temperature.

Keywords: $BaTi_4O_9$; Dielectric properties; Microstructure-final; Microwave dielectrics; Powders-chemical preparation; Sintering

1. Introduction

Recently, the development of commercial wireless technologies makes rapid progress because of the improved characteristics of dielectric resonators in microwave ranges. Requirements of the dielectric resonators are combined with a high dielectric constant (ε_r) for possible size miniaturization (physical length of a dielectric resonator $\sim 1/\sqrt{\varepsilon_r}$), a high unloaded quality value (Q, where Q is inversely to dielectric loss tanδ) for reducing the losses of the microwave devices, and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stable circuits.[1]

A number of researchers have reported that TiO_2-rich compounds with Ti/Ba = 4 or 4.5 (i.e. $BaTi_4O_9$ or $Ba_2Ti_9O_{20}$) exhibit suitable microwave dielectric properties for microwave dielectric application.[2–4] However, the compositional and structural fluctuations due to the reduction of Ti^{4+} to Ti^{3+} often make a severe degradation of dielectric properties, since the conventional sintering temperatures of ceramics are as high as 1400 °C[5] In addition, the formation of second phase such as hollandite ($BaAl_2Ti_6O_{15}$) phase caused by ball milling with $A1_2O_3$ media reduced the dielectric properties of $BaTi_4O_9$ ceramics.[6] From the above viewpoints, the single phase and high homogeneous $BaTi_4O_9$ ceramics at lower sintering temperature are needed to improve and control the dielectric properties. In the past, researchers made effort in stabilizing the $BaTi_4O_9$ phase and improving the dielectric properties with different additives,[7–14] while fewer studies dedicated on lowering the sintering temperature of $BaTLO_9$ ceramics.[15–18] There are three common methods used in reducing the sintering temperature of dielectric ceramics: low-melting glass addition,[15] chemical processing,[16–18] and using starting materials with smaller particle sizes. Takada et al. examined the effect of glass additions on the sintering temperature and dielectric properties of $BaO–Ti0_2$ based ceramics.[17] They found that dielectric properties degraded rapidly as increase of glass amount, although the sintenng temperature of ceramics actually and effectively lowered. Recently, the $BaTi_4O_9$ ceramics have prepared at low temperature (1250 °C) via citrate route by J. H. Choy and coworkers,[18] and exhibited good microwave dielectric properties of $\varepsilon_r \sim 36$, $Q \sim 4900$ at 10.3 GHz and $\tau_f \sim 16$ ppm/°C.[18]

* Corresponding author.
E-mail address: mhweng@ckmail.ncku.edu.tw (M.H. Weng).

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In this paper, we reported a modified citrate route to prepare the $BaTi_4O_9$ ceramics, since the starting materials were different to that in Ref. 18. The main goals of this investigation were the development of inexpensive polymeric precursor route based on Pechini process[19] for preparing the $BaTi_4O_9$ powder and the study of the microwave dielectric properties of sintered $BaTi_4O_9$ ceramics. The resultant densification and microwave dielectric properties were analyzed.

2. Experimental procedures

2.1. Sample preparation

The starting reagents used were high-purity (>99.9%): $BaCO_3$ and $Ti(OCH(CH_3)_2)_4$. Fine $BaCO_3$ powder which could be dispersed easily was chosen. Preparation sequence of $BaTi_4O_9$ powders using polymeric precursor route (Pechini methods) was shown in Fig. 1. Proper amount of ethylene glycol ($C_2H_6O_2$) was heated to 50 °C and then added slowly with $Ti(OCH(CH_3)_2)_4$. After the milk-like solution stirred to become colorless, a given quantity of citrate acid ($C_6H_8O_7$–$2H_2O$) was added and stirred to promote the dispersion of the gels.[18] Desired stoichiometry $BaCO_3$ powder was then added slowly and highly dispersed by mechanical stirring, as the temperature increased from 50 to 150 °C for 2 h. The pH value was 3.7 as mixtures became clear and light yellow solution. To prepare $BaTi_4O_9$ powders, the polymeric precursor were further heating at 300 °C for 1–2 h resulted in the dark colored, amorphous citrate gels with low viscosity. The gels were calcined at 600–900 °C for 3 h with a step of 50 °C. The calcined powder was then remilled again with 3 wt.% of a 10% solution of poly vinyl alcohol (PVA) as the binder. Pellets with 11 mm diameter and 5 mm thick were pressed by uniaxial pressing. After debinding, these pellets were sintered at the temperature of 1200–1300 °C for 3 h. For comparison, $Ba_2Ti_9O_{20}$ ceramics prepared by the conventional mixed oxides method were sintered at temperatures of 1200–1350 °C for 3 h. The heating and cooling rates of the samples were 10 °C/mm in both cases.

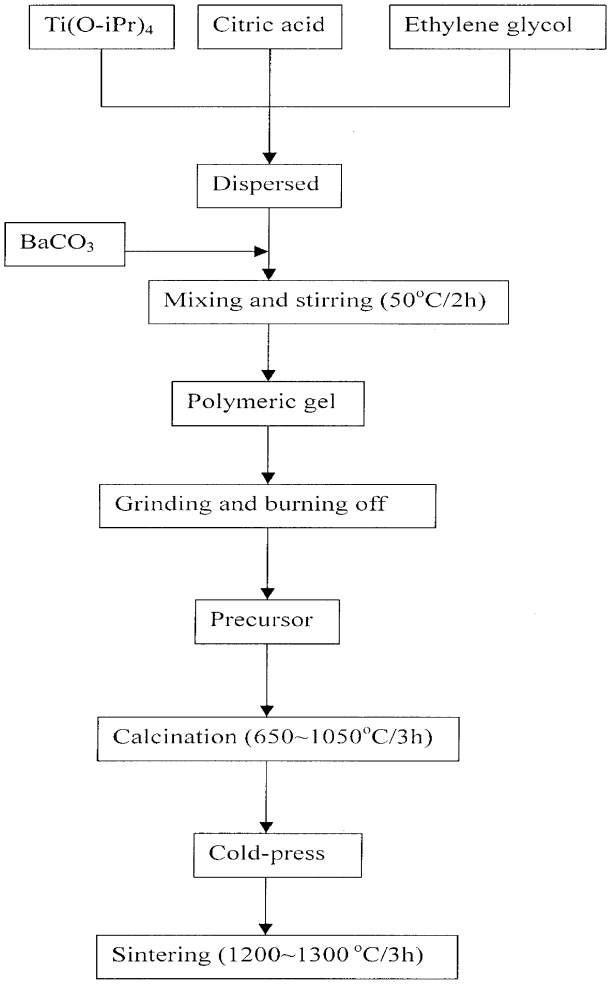

Fig. 1. Preparation sequence of $BaTi_4O_9$ powders using the citrate route.

2.2. Characteristics analysis

The crystalline phases of the calcined powder and the sintered ceramics were identified by X-ray diffraction pattern analysis (XRD, Rigaku D/Max III. V) using Cu-K_α radiation for 2θ from 2 to 60 °. The scanning rate was 4°/mm. Microstructural observation of the calcined powder and the sintered surface was performed by scanning electron microscopy (SEM, Jeol, JEL-6400). The bulk densities of the sintered pellets were measured by the Archimedes method. The average grain sizes were calculated from the line intercept method.

The dielectric constants (ε_r) were calculated by the sizes of sample and the frequency of TE_{011} mode at 6 GHz using the Hakki–Coleman method.[20] The unloaded quality values Q at microwave frequencies were measured by the dielectric resonator method improved by Kabayashi.[21] Since the $Q\times f$ value keeps constant in the microwave region, the unloaded quality values were expressed as $Q\times f$ values. The temperature coefficient of resonant frequency (τ_f) at microwave frequency was measured in the temperature range from 20 to 80 °C, and calculated by Eq. (1),

$$\tau_f = (f_{80} - f_{20})/(60 \times f_{20}) \times 10^6 \quad (\text{ppm}/^\circ\text{C}) \tag{1}$$

where f_{20} and f_{80} are $TE_{01\delta}$ resonant frequency at 20 and 80 °C.

A system including a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement of dielectric properties.

3. Results and discussion

3.1. Crystallization and particle morphology

Fig. 2 shows the X-ray diffraction patterns of the $BaTi_4O_9$ powders after heating the polymeric precursor at 650–850 °C for 3 h. Calcined powders were in an amorphous state below 700 °C. The main reflections of $BaTi_4O_9$ phase started to be visible clearly above 750 °C. As calcining the $BaTi_4O_9$ powders at 800 °C, $BaTi_4O_9$ phase is present as the main crystalline phase in association with $BaTi_5O_{11}$, and $Ba_2Ti_9O_{20}$ as minor phases. The intensity of main peaks increased remarkably with the increase of calcined temperature. Well crystalline phase of $BaTi_4O_9$ was most complete at 850 °C and each peak was well agreed with those in JCPDS 34-70.

Fig. 3 shows particle morphology of $BaTi_4O_9$ powders after calcining at 800 and 850 °C. The powders calcined at 800 °C were nearly round shaped particles with a fine diameter of 100–200 nm and well dispersion. However, the powders calcined at 850 °C showed fine particles and some agglomeration. A dense and rigid resin intermediate of citric acid and ethylene glycol caused an unavoidable particle agglomeration during firing.[19] Fig. 4 shows the particle size distribution of $BaTi_4O_9$ powders after calcining at 800 and 850 °C. Most particle sizes of $BaTi_4O_9$ powders after calcining at 800 °C were confirmed to distribute from 100 to 300 nm, and few agglomeration particles are 2–5 μm. With increasing the calcined temperature, the amount of agglomeration also increased. The results of particle size distribution suggested that the fine particles were slightly necked each

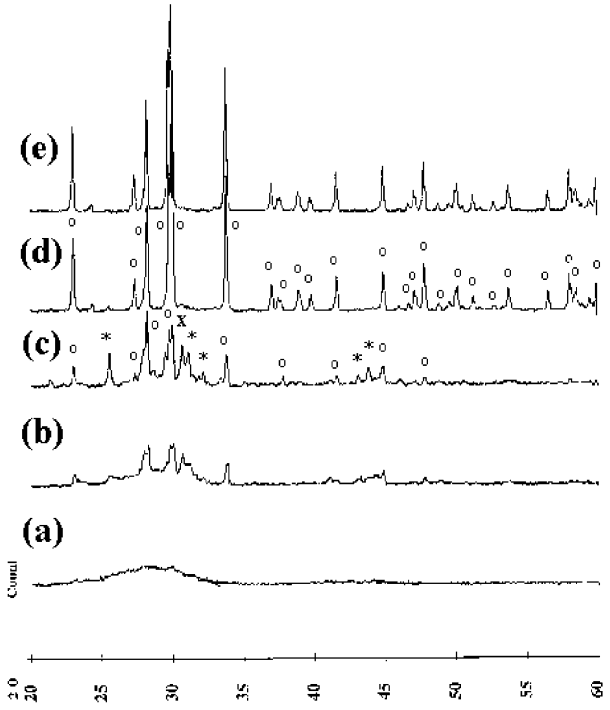

Fig. 2. X-ray diffraction patterns of the $BaTi_4O_9$ powders after heating the polymeric gel at different temperature for 3 h (a) 650 °C (b) 700 °C (c) 750 °C (d) 800 °C and (e) 850 °C (o: $BaTi_4O_9$; x: $Ba_2Ti_9O_{20}$; *: $BaTi_5O_{11}$).

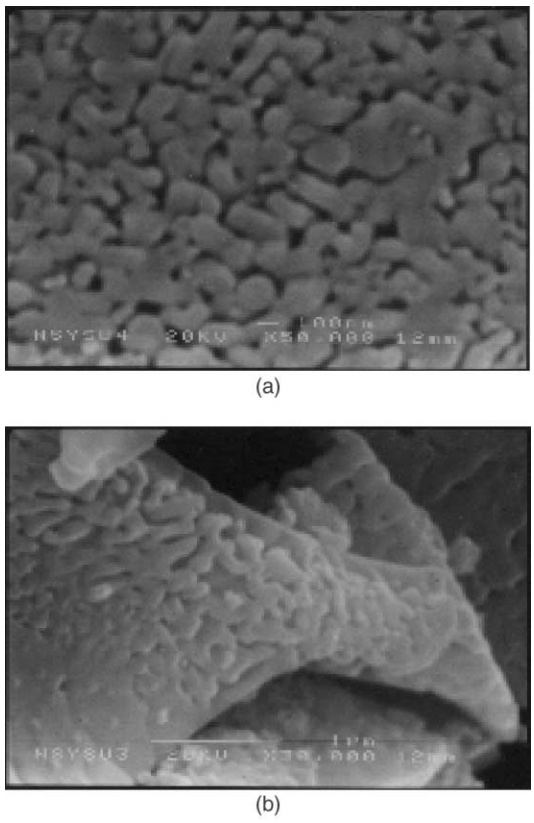

Fig. 3. Particle morphology of $BaTi_4O_9$ powders after heating at (a) 800 and (b) 850 °C: (a) ×30,000 and (b) ×50,000.

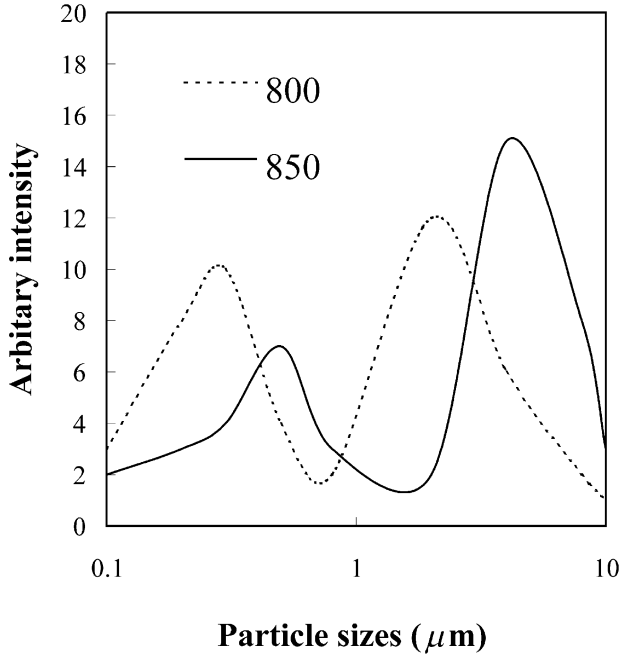

Fig. 4. Typical particle size distribution data.

other and started to react at such a low temperature of 850 °C.

X-ray diffraction patterns of $BaTi_4O_9$ ceramics prepared by the polymeric precursor route and sintered at 1200, 1250 and 1300 °C for 3 h are shown in Fig. 5. The diffraction patterns of $BaTi_4O_9$ ceramics showed a single orthorhombic phase and well crystalline. Fig. 6 shows X-ray diffraction patterns of $BaTi_4O_9$ ceramics prepared by conventional mixed oxide method sintered at the same temperatures for comparison. The main reflections of $BaTi_4O_9$ phase started to be visible clearly above 1200 °C. As sintered $BaTi_4O_9$ ceramics at 1250 °C, $BaTi_4O_9$ phase is present as the main crystalline phase in association with $Ba_4Ti_{13}O_{30}$ and $Ba_2Ti_9O_{20}$ as minor phases. Increasing the temperature further to 1300 °C, single-phase $BaTi_4O_9$ still cannot synthesized and the X-ray patterns of $Ba_2Ti_9O_{20}$ are still detected.

3.2. Densification and microstructures

The relative theoretical densities of $BaTi_4O_9$ ceramics prepared by the polymeric precursor route and the conventional mixed oxides method as a function of their sintering temperatures were indicated in Fig. 7. Only 85 and 93% theoretical densities were obtained for $BaTi_4O_9$ ceramics prepared by the conventional method at 1200 and 1300 °C, respectively. The theoretical densities of sintered samples prepared by the polymeric precursor route increased from 91 to 95.3% as the sintering temperature increased from 1200 to 1250 °C and then slightly decreased (94% at 1300 °C). The ceramics prepared by polymeric precursor route had the ability to dense more effectively at lower sintering temperature. The reason was that the fine and well dispersive powders prepared by chemical method have high reactive and have been as suggested by many researchers.[16–18]

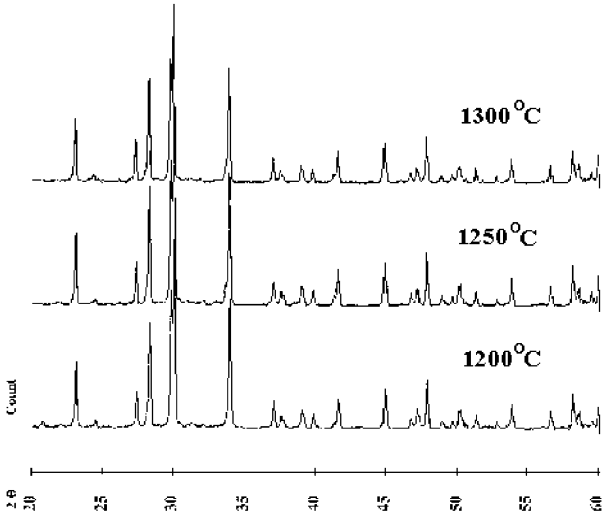

Fig. 5. X-ray diffraction patterns of $BaTi_4O_9$ ceramics sintered at 1200, 1250 and 1300 °C for 3 h.

Fig. 8 illustrates the SEM micrographs of $BaTi_4O_9$ ceramics sintered at 1200 and 1250 °C for 3 h in air. The grain size of $BaTi_4O_9$ ceramics sintered at 1200 °C had growed and revealed grain size was 2–6 μm, although some pores were still residual in the grain boundary. The grain growth at such a low sintering temperature was also due to the ultra fine particles and larger reactive surfaces.[18] As the increase of sintering temperature at sintered at 1250 °C, the grain sizes of $BaTi_4O_9$ ceramics increased slightly. Fewer pores were residual at grain boundaries or triple points and no cracks were appeared. In addition, the surface and interiors of the sintered $BaTi_4O_9$ pellets were pale yellow uniformly. The results suggested there were no reduction in the

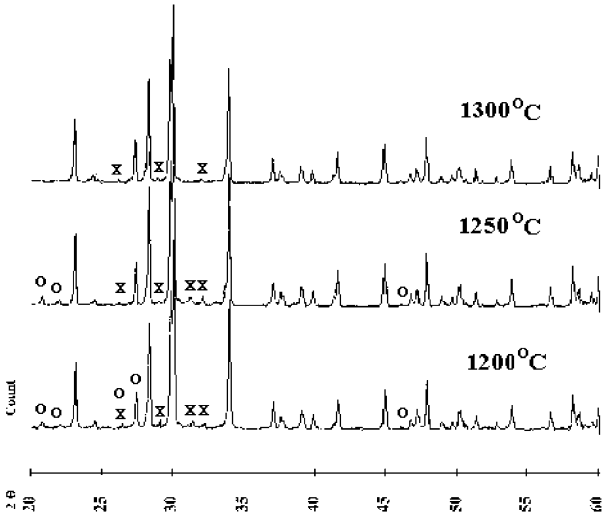

Fig. 6. X-ray diffraction patterns of $BaTi_4O_9$ ceramics prepared by conventional mixed oxide method sintered at 1200, 1250 and 1300 °C for 3 h. (o: $Ba_4Ti_{13}O_{30}$; x: $Ba_2Ti_9O_20$).

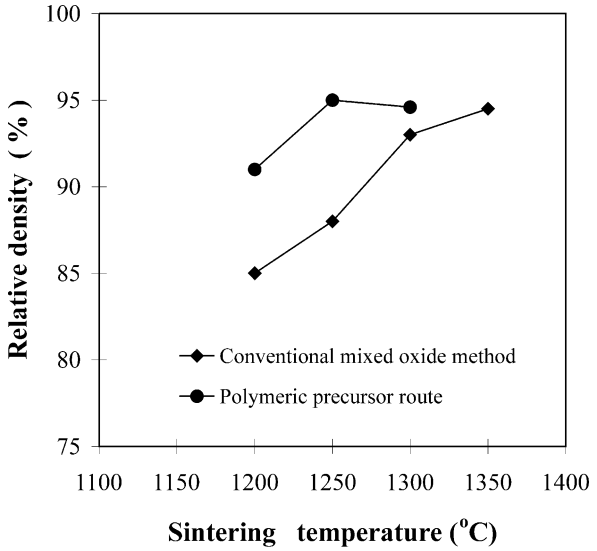

Fig. 7. The relative densities of $BaTLi_4O_9$ ceramics as functions of sintering temperatures with different prepared methods.

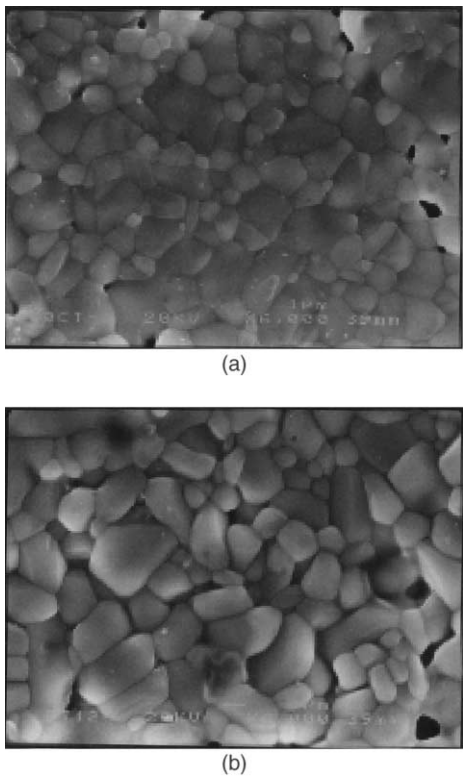

Fig. 8. Scanning electron micrographs of $BaTi_4O_9$ ceramics sintered at (a) 1200 °C and (b) 1250 °C for 3 h in air (×6000).

samples since the processing temperatures were much lower than 1400 °C.[5]

3.3. Microwave dielectric properties

Physical and dielectric properties of $BaTi_4O_9$ ceramics as a function of sintering temperature were shown in Table 1. The ε_r values increase from 30 to 35.6 with the increase of sintering temperatures from 1200 to 1250 °C owing to the increase in the densities. In general, higher density results in higher dielectric constant owing to lower porosity (the dielectric constant of pore equals 1.0).[1] The $Q\times f$ values of $BaTi_4O_9$ ceramics revealed 32,100–42,600 as the sintering temperatures at 1200 and 1250 °C, respectively. Increasing the sintering temperature to 1300 °C decreased the $Q\times f$ values. The results were close to the ones prepared by citrate route.[18] The τ_f values in $BaTi_4O_9$ system decreased with increase of sintering temperature and showed the minimum value of 3 ppm/°C at sintering temperature of 1300 °C.

Table 1
Physical and dielectric properties (measured at 6 GHz) of $BaTi_4O_9$ ceramics as a function of sintering temperature for 3 h in air.

ST (°C)	Prepared method	*D* (g/cm^3)	*GS* (μm)	ε_r	$Q\times F$ (GHz)	$\cdot_f$ (ppm/°C)
1200	C	4.09	2–6	30.3	32 100	16
1250	C	4.23	3–8	35.6	42 600	12
1300	C	4.16	3–9	34.9	40 500	3
1200	M	3.86	1–3	25.5	16 300	–
1250	M	4.12	2–5	33.2	23 800	18
1300	M	4.19	3–6	34.6	32 600	–

ST: sintering temperature, *D*: bulk density, *GS*: grain sizes, –: not available, C: chemical method, M: conventional mixed oxide method.

Additional properties of $BaTi_4O_9$ ceramics prepared by conventional mixed oxide method were also shown in Table 1. Comparing to the dielectric properties in two different prepared methods, the $Q\times f$ values of $BaTi_4O_9$ ceramics prepared by the polymeric precursor route were relatively higher than ones prepared by another method. Many reason for microwave dielectric losses are suggested including intrinsic loss and extrinsic loss.[22] The intrinsic losses were mainly caused by the lattice vibration modes while the extrinsic losses were dominated by second phases, oxygen vacancies, grain sizes and densification/porosity.[22] At the same sintering temperature, the $Q\times f$ values of $BaTi_4O_9$ ceramics prepared by the polymeric precursor route were higher than another ones due to more densification. However, even the similar densities of two cases, the $Q\times f$ values of $BaTi_4O_9$ ceramics prepared by the polymeric precursor route were still higher than another ones. Grain sizes were suggested to affect the $Q\times f$ values of dielectric resonators.[22] However, the $Q\times f$ values demonstrated large difference in two cases while the grain sizes remained similar (2–8μm). Referring to Figs. 5 and 6, it was believed that the existence of second phases (such as $Ba_4Ti_{13}O_{30}$) in the conventional mixed oxide method caused the decrease of the $Q\times f$ values at such low sintering temperatures. Another, the improvement of Q values was also suggested as the advantages of high homogeneous and high purity powder prepared by the polymeric precursor route.[18]

4. Conclusions

In this study, single phase $BaTi_4O_9$ powders and ceramics were successfully synthesized at low processing temperature by the polymeric precursor route and the microwave dielectric properties of $BaTi_4O_9$ ceramics were developed. The conclusions were followed as:

1. Well crystalline $BaTi_4O_9$ powders could be prepared by the polymeric precursor route and a particle size of 100–300 nm was observed from the thermal decomposition of amorphous gel precursor at 800 °C.
2. Sintered $BaTi_4O_9$ ceramics achieved a 95.3% theoretical density at 1250 °C and well grain growth of 3–8 μm.
3. The dielectric properties of $BaTi_4O_9$ ceramics showed dielectric constant of 35.6; high $Q\times f$ value of 42,600 and the temperature coefficient of resonant frequency of 12 ppm/°C.

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