



DR HONGTAO YU (Orcid ID : 0000-0002-4445-3170)

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## **Phase evolution and microwave dielectric properties of BaTi<sub>4</sub>O<sub>9</sub> ceramics prepared by reaction sintering method**

Ting Luo, Lei He, Huan Yang, Hongtao Yu\*

Corresponding Author Email ID: htyu\_76@163.com

School of Materials Science and Engineering, Southwest University of Science and Technology, 621010, Mianyang, P.R. China

### **Abstract**

BaTi<sub>4</sub>O<sub>9</sub> microwave dielectric ceramics were prepared by reaction sintering method using BaCO<sub>3</sub> and TiO<sub>2</sub> as raw materials. The phase evolution and the chemical reactions were proposed based on the X-ray diffraction results with

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sintering temperature. The microstructure characteristics were observed using scanning electron microscopy and energy dispersive spectrometer. The compact ceramics with a single phase of  $\text{BaTi}_4\text{O}_9$  could be prepared successfully by reaction sintering method, exhibiting optimum microwave dielectric properties: a dielectric constant of 36.9, a high quality factor of 52735 (at 7.5GHz) and a near zero temperature coefficient of resonant frequency of 5.8 ppm/ $^{\circ}\text{C}$ , after sintering at 1200  $^{\circ}\text{C}$  for 6h.

## **Keywords**

$\text{BaTi}_4\text{O}_9$ ; Reaction sintering; Phase; Microwave dielectric properties

## **Introduction**

During past forty years, microwave dielectric ceramics have made enormous progress for achieving the higher speed and producing miniature size components in the commercial wireless technologies such as mobile phone and global position systems (GPS), due to their high dielectric constant and high quality factor with good temperature stability [1-3].

Barium tetra-titanate ( $\text{BaTi}_4\text{O}_9$ ) is a candidate material for dielectric resonators in microwave telecommunication and satellite broadcasting, because of its good microwave dielectric properties: a high dielectric constant ( $\epsilon_r=39$ ), a

good quality factor ( $Q_f=40000$  at 4 GHz) and a temperature coefficient of resonant frequency ( $\tau_f=14\text{ppm}/^\circ\text{C}$ ) [4]. To lower the sintering temperature ( $>1300^\circ\text{C}$ ) and improve the performances of  $\text{BaTi}_4\text{O}_9$  ceramics, many works were carried out by researchers. Kim et al. lowered the sintering temperature to  $900^\circ\text{C}$  using Zn-B-O glass as sintering aid and obtained good microwave dielectric properties :  $\epsilon_r=33$ ,  $Q_f=27000$  (at 7GHz) and  $\tau_f=7\text{ppm}/^\circ\text{C}$  [5]. Choy and Han used citrate route to synthesis the powder and prepared the ceramic of  $\epsilon_r=36$ ,  $Q_f=50470$  (at 10.3 GHz) and  $\tau_f=16\text{ppm}/^\circ\text{C}$  after sintering at  $1250^\circ\text{C}$  [6]. Weng et al. produced  $\text{BaTi}_4\text{O}_9$  ceramics of  $\epsilon_r=35.6$ ,  $Q_f=42,600$  (at 6 GHz) and  $\tau_f=12\text{ppm}/^\circ\text{C}$  by the polymeric precursor method and sintered at  $1250^\circ\text{C}$  [7].

The reaction sintering process is a simple and effective process in preparing functional ceramics due to withdrawing calcination and reducing grinding, compared with the conventional solid state method. To date, many electric-functional ceramics were prepared by this method successfully, such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,  $\text{ZnNb}_2\text{O}_6$ ,  $\text{BaTi}_9\text{O}_{20}$  and  $\text{Li}_2\text{ZnTi}_3\text{O}_8$  [8-11]. Liou et al. used reaction sintering method to prepare  $\text{BaTi}_4\text{O}_9$  ceramic with high-sintered density (98.2-99.5% of theoretical value) for pellets sintered at  $1200\text{-}1280^\circ\text{C}$  for 2-6 h in 2005 [12]. Two years later, the same authors investigated the effects of dopants on  $\text{BaTi}_4\text{O}_9$  ceramics prepared by reaction sintering process and reported excellent microwave dielectric properties in  $\text{BaTi}_4\text{O}_9$  doped with 0.1 wt %  $\text{MnO}_2$ :  $\epsilon_r=37.1$ ,  $Q_f=51200$  (at 7 GHz) and  $\tau_f=0\text{ppm}/^\circ\text{C}$  [13]. Unfortunately, no phase evolution was studied during the preparation process of  $\text{BaTi}_4\text{O}_9$  ceramics

using reaction sintering method. As reported, the  $\text{BaTi}_4\text{O}_9$  ceramics were usually accompanied with some minor phases such as  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$  [14]. Weng et al. proposed that  $\text{BaTi}_4\text{O}_9$  phase associated with  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phases were obtained after sintered at 1250 °C for 3 h by the conventional mixed oxide method.  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was still detected even after 3 h sintering at 1300 °C [7]. Xu et al. reported that a mixture of  $\text{BaTi}_4\text{O}_9$ ,  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$  and  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phases were observed in the 1100 °C for 4 h heated  $\text{BaTi}_4\text{O}_9$  precursor prepared by a sol–gel method using EDTA as a chelating agent. Single phase  $\text{BaTi}_4\text{O}_9$  cannot be synthesized even after heating the precursors for 2 h at 1200 °C.  $\text{Ba}_2\text{Ti}_9\text{O}_{20}$  phase was still detected [15]. Therefore, the occurrence of reactions among the phases during the sintering process is inevitable, which degrades the reliability of the processing for preparing the  $\text{BaTi}_4\text{O}_9$  materials.

As well known, microwave dielectric properties depend strongly on phase compositions and microstructure characteristics controlled by the process in ceramics. Thus, we studied the evolutions of phase and microstructure in  $\text{BaTi}_4\text{O}_9$  ceramics prepared by reaction sintering process to reveal the relationship between the microwave dielectric properties and the reaction sintering process in the present work.

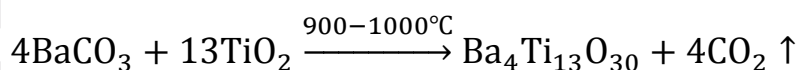
## Experimental process

Highly pure  $\text{BaCO}_3$  (99.9%) and  $\text{TiO}_2$  (99.8%) as raw materials were weighted according to the molar ratio of  $\text{BaO}/\text{TiO}_2=1/4$ , and 0.1 wt%  $\text{MnO}_2$  (>99%) and 0.5 wt%  $\text{SiO}_2$  (99.9%) as modifiers on the base of the report by Liou [13]. The above three kind materials were mixed and milled in planetary mills with distilled water for 4 h. The dried mixed powders were mixed with 10 wt% PVA solution as binder, and then pressed into green pellets with a diameter of 10 mm and a thickness of around 6 mm under a pressure of 160 MPa. These pellets were sintered at different temperatures for various time with a heat rating of 2 °C/min., after de-binding at 650 °C for 2h.

Powder X-ray diffraction (XRD, D/max400, Rigaku, Japan) and energy dispersive spectrometer (EDS, GENESIS-2000, EDAX, U.S.A.) were used to confirm the phase structure of the samples. The microstructure characteristics were observed using scanning electron microscopy (SEM, TM1000, Hitachi, Japan). The bulk densities of the specimens were measured by the liquid Archimedes method. The dielectric constant ( $\epsilon_r$ ) and the quality factor ( $Q_f$ ) values at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method with a vector-net-work analyzer (Agilent E5071C). The temperature coefficient of resonant frequency ( $\tau_f$ ) was obtained by measuring the resonant frequency of the  $\text{TE}_{01\delta}$  mode at 20 °C and 80 °C

## Results and Discussions

Fig. 1 shows the XRD patterns of the green pellets heated at different temperatures for 1 h. After heating at 900 °C, the pellets consisted with four phases, BaCO<sub>3</sub>, TiO<sub>2</sub>, Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub> and BaTi<sub>4</sub>O<sub>9</sub>. When the temperature increased to 1000 °C, the phase of BaCO<sub>3</sub> disappeared. It could be proposed that all BaCO<sub>3</sub> might reaction with other phases. The intensities of BaTi<sub>4</sub>O<sub>9</sub> and Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub> peaks increased, whereas the intensity of TiO<sub>2</sub> peaks at 2θ=35.98 and 54.22 decreased obviously. Furthering elevating the temperature to 1100 °C, only a phase of BaTi<sub>4</sub>O<sub>9</sub> was found in the sample. The inset in Fig.1 shows the variation on the BaTi<sub>4</sub>O<sub>9</sub> content as a function of heated temperature. The percentage of the BaTi<sub>4</sub>O<sub>9</sub> phase was calculated by the Rietveld refinement method [16-18]. It is clear that the content of BaTi<sub>4</sub>O<sub>9</sub> increased with temperature increasing. According to the XRD results, BaCO<sub>3</sub> reacted with TiO<sub>2</sub> to produce BaTi<sub>4</sub>O<sub>9</sub> and Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub> at 900 °C. With increasing temperature, the contents of BaTi<sub>4</sub>O<sub>9</sub> and Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub> increased. Thus, the continued reaction between BaCO<sub>3</sub> and TiO<sub>2</sub> led to the formations of BaTi<sub>4</sub>O<sub>9</sub> and Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub>. After heating at 1100 °C, the residual TiO<sub>2</sub> reacted with Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub> to form BaTi<sub>4</sub>O<sub>9</sub>. Thus, only a single phase of BaTi<sub>4</sub>O<sub>9</sub> was detected. According to above illustrations, the chemical reactions during the heat-treatment progress could be proposed as followed:



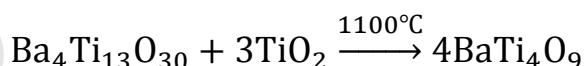
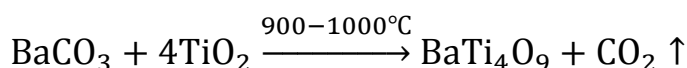


Fig. 2 illustrates the XRD patterns of BaTi<sub>4</sub>O<sub>9</sub> ceramics sintered at different temperatures for 3h. Some reports showed that the compact ceramics of BaTi<sub>4</sub>O<sub>9</sub> prepared by conventional oxide route or wet-chemical method exhibited some minor crystal phases of Ba<sub>4</sub>Ti<sub>13</sub>O<sub>30</sub> and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>, which implied the occurrence of reaction during the process. Thus, the degradation of the reliability of the processing for preparing the BaTi<sub>4</sub>O<sub>9</sub> materials was inevitable. However, when the sintering temperature increased or the soaking time was prolonged, the phase composition in the sample did not change in the present work. Only a single phase of BaTi<sub>4</sub>O<sub>9</sub> was observed in all specimens based on the XRD results as shown in Fig. 2, which means no decomposition reactions to produce other phases during the sintering progress. Thus, it could be proposed that reaction sintering method was an efficient route to prepare microwave dielectric ceramics with a single phase of BaTi<sub>4</sub>O<sub>9</sub>.

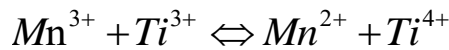
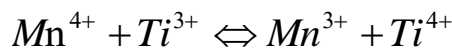
The influence of sintering temperature and soaking time on the density of BaTi<sub>4</sub>O<sub>9</sub> ceramics is plotted in Fig.3. The density increased with increasing sintering temperature due to the elimination of pore as observed in SEM result shown in Fig. 4 and saturated at 1200 °C with a value of 4.456 and 4.503 g/cm<sup>3</sup> for 3 and 6 h, respectively. Further increasing sintering temperature to 1300 °C, the density decreased slightly, which could be attributed to the abnormal large

grain as shown in the area 3 of Fig. 4 (C). High sintered density of >96% of theoretical value  $4.533 \text{ g/cm}^3$  (PDF No.77-1565) could be obtained in the temperature range of 1150-1300 °C no matter what soaking time was. Especially, when the samples were sintered at 1200 °C for 6h, the highest relative density of 99.3% was achieved. Thus, the dense  $\text{BaTi}_4\text{O}_9$  ceramics could be prepared by reaction sintering process easily without the calcination stage. The similar result was also found in the report by Liou [12].

To observe the evolutions of microstructure and phase in  $\text{BaTi}_4\text{O}_9$  ceramics prepared by reaction sintering method, the scanning electronic microscopy (SEM) and the energy disperse spectra (EDS) were used. The results were illustrated in Fig. 4 and 5. Some pores were observed in the sample sintered at 1100 °C, which contributed to the low density. With increasing temperature, pores disappeared accompanied with the growth of grains and the increase in the density. It is obvious that rod-shaped grains dominated the microstructure characteristics from the observation in Fig. 4 and the amount of these rod-shaped grains increased at higher sintering temperature or longer soaking time. These rod-grains were also found by other researchers. They attributed the rod-grains to the phase of  $\text{BaTi}_4\text{O}_9$  [13]. We used EDS to confirm this as shown in Fig. 5. Other irregular grains like the area 1, 3 and 4 in the Fig. 4 were also confirmed to be  $\text{BaTi}_4\text{O}_9$ . The observations in the EDS were in line with the XRD results plotted in Fig. 2. Fig. 5 shows the EDS of the different grains as shown in the areas in Fig. 4. It was obvious that the ratio of Ti/Ba was clear to 4



for different grains, which implied that the ceramics exhibited a single phase of BaTi<sub>4</sub>O<sub>9</sub>. Only the amount of oxygen (O) decreased with sintering temperature. As known, titanates require high temperature for sintering, which results in oxygen vacancies in the lattice [19, 20]. The vacancies lead to the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>, which degrades the quality factor. To overcome the effect of the vacancies, Mn<sup>4+</sup> is usually used as modifier as followed



Thus, Mn<sup>4+</sup> can control the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>, acting as a compensator for defect equilibrium helping to maintain Ti<sup>4+</sup> during sintering [21, 22].

Fig. 6 illustrates the effects of sintering temperature and soaking time on the dielectric constant and the quality factor in BaTi<sub>4</sub>O<sub>9</sub> ceramics. Accordingly, microwave dielectric properties have strong dependences on intrinsic factors, such as ionic polarization and lattice vibration modes, as well as extrinsic factors like relative densities, grain morphology and porosity [21]. Based on the foundation in the XRD patterns (Fig. 1 and 2), all samples exhibited only a single phase of BaTi<sub>4</sub>O<sub>9</sub> when sintering temperature was no less than 1150 °C. Thus, it could be proposed that the dielectric constant and the quality factor were dominated by the extrinsic factors, such as relative densities. It is obvious that both the dielectric constant and the quality factor had a similar tendency to the density with sintering temperature and soaking time as shown in Fig. 3. The

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dielectric constant was in a range of 36.7-36.9 when the bulk density was larger than  $4.35\text{g/cm}^3$ , while the value was 34.1 or 34.7 in the sample sintered at  $1150^\circ\text{C}$  for 3h or 6h due to its relatively low density ( $< 4.25\text{g/cm}^3$ ) shown in Fig. 3. Similarly, the high quality factors ( $>45000$  at 7.5 GHz) were found in the ceramics sintered at a range of  $1200\text{-}1250^\circ\text{C}$ . The maximum value was 51867 or 53735 in the ceramics sintered at  $1200^\circ\text{C}$  for 3h or 6h, respectively. Both high quality factors might be attributed to the homogeneous grains size and distribution (Fig. 4 (b) and (d)), too. However, some pores could be observed in the samples sintered at  $1100^\circ\text{C}$  as shown in the SEM images, which might lead to low quality factor values, 31226 and 33220 for 3h and 6h respectively. Some abnormal large grains found in the samples sintered at  $1300^\circ\text{C}$  increased the microwave scattering, leading to the reduction in the quality factor.

The temperature coefficients of resonant frequency shifted negatively with sintering temperature as shown in Fig. 6. Considering the same phase of  $\text{BaTi}_4\text{O}_9$  in all samples sintered at  $1100\text{-}1300^\circ\text{C}$ , the variations of  $\tau_f$  value might depend strongly on the variations of the microstructure characteristics with sintering conditions, such as grain size, relative density, porosity, oxygen vacancies and so on [21]. After sintering at  $1200^\circ\text{C}$  for 6 h, the ceramic exhibited a  $\tau_f$  value of  $5.8\text{ ppm}/^\circ\text{C}$ .

The characteristics of  $\text{BaTi}_4\text{O}_9$  ceramics prepared by various solid state methods are listed in Table I [23]. Both samples obtained from reaction sintering had higher quality factor than that from conventional route. As known, there are two grinding steps in conventional route, whereas only one in reaction sintering method. Thus, the contamination from grinding would be less in reaction sintering route. As a result, a higher quality factor was obtained. Additionally, the sintering temperature in reaction sintering method was obviously lower than in conventional route. Another important reason is that the particles have higher reactivity. In former process, the particles reacted with each other and sintered simultaneously, which would lower the sintering temperature. This reduction had been found in some microwave dielectric ceramics. Compared with the report by Liou [12], the sintering temperature was low in our work, which might be due to difference particle sizes and  $\text{SiO}_2$  additive.

## Conclusion

In this work, we used reaction sintering method to prepare the microwave dielectric ceramics with a single phase of  $\text{BaTi}_4\text{O}_9$  successfully. The chemical reactions were proposed during the process. Firstly,  $\text{BaCO}_3$  and  $\text{TiO}_2$  reacted with each other to produce  $\text{BaTi}_4\text{O}_9$  and  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$ . With evaluating heating temperature, the samples consisted with  $\text{BaTi}_4\text{O}_9$ ,  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$  and  $\text{TiO}_2$ , simultaneously  $\text{BaCO}_3$  consumed completely. Further increasing temperature to  $1100^\circ\text{C}$ ,  $\text{Ba}_4\text{Ti}_{13}\text{O}_{30}$  reacted with the residual  $\text{TiO}_2$  to form  $\text{BaTi}_4\text{O}_9$ . The

compact ceramics exhibiting a single phase of  $\text{BaTi}_4\text{O}_9$  were obtained after sintering at 1150 to 1300 °C. The microwave dielectric properties depended on the microstructure evolution, which was similar to the variation in relative density with sintering temperature. When the pellets were sintered at 1200 °C for 3 h or 6h, the ceramics had optimum microwave dielectric properties:  $\epsilon_r=36-37$ ,  $Q_f>50000$  (at 7.5GHz) and near zero  $\tau_f$  values.

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## Figure Captions

Fig. 1 XRD patterns of green pellets heated at 900 °C (a), 1000 °C (b) and 1100 °C for 1h

Fig. 2 XRD patterns of ceramics sintered at 1150 °C, 1200 °C, 1250 °C and 1300 °C for 3h

Fig. 3 Bulk density of BaTi<sub>4</sub>O<sub>9</sub> ceramics vs sintering temperature and soaking time

Fig. 4 SEM images of BaTi<sub>4</sub>O<sub>9</sub> ceramics sintered at (a): 1100 °C for 3h, (b): 1200 °C for 3h, (c): 1300 °C for 3h, and (d): 1200 °C for 6h

Fig. 5 EDS of the areas in Fig. 4

Fig. 6 Effect of sintering temperature and soaking time on microwave dielectric properties of BaTi<sub>4</sub>O<sub>9</sub> ceramics prepared by reaction sintering methods



Table I Preparation and performance of BaTi<sub>4</sub>O<sub>9</sub>-based ceramics

Prepared by	Ref. 22	Ref. 13	This work
Processing	Conventional method with 0.1 mol MnO <sub>2</sub> + CaCO <sub>3</sub>	Reaction sintering with 0.1 wt% MnO <sub>2</sub>	Reaction sintering with 0.1 wt% MnO <sub>2</sub> + 0.5 wt% SiO <sub>2</sub>
Calcination	1075 °C for 4 h	None	None
Sintering	1375 °C for 4h	1300 °C for 4 h	1200 °C 6 h
ε <sub>r</sub>	33	37.1	36.9
Q <sub>f</sub>	46500 (at 9,3GHz)	51000 (at 7GHz)	53757 (at 7.5GHz)
τ <sub>f</sub> (ppm/°C)	5	0	5.8

