

Sintering BaTi₄O₉/Ba₂Ti₉O₂₀-based ceramics by glass addition

Chien-Min Cheng^{a,*}, Cheng-Fu Yang^{b,*}, Shi-Hong Lo^b, Tseung-Yuen Tseng

^aDepartment of Electronic Engineering, National Chiao Tung University, Hsinchu, Taiwan, ROC

^bDepartment of Electronic Engineering, Chinese Air Force Academy PO Box 90277-4, Kangshan, Kaohsiung, Taiwan 82012, ROC

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Abstract

After calcining BaCO₃ + 4TiO₂ mixed powder at 1150°C for 2 h, BaTi₄O₉ is the major phase, Ba₄Ti₁₃O₃₀ and BaTi₅O₁₁ are minor phases. After calcining 2BaCO₃ + 9TiO₂ mixed powder at 1200°C for 10 h, Ba₂Ti₉O₂₀ is the major phase, BaTi₄O₉ and BaTi₅O₁₁ are the minor phases. The calcining powders are used as the BaTi₄O₉ and Ba₂Ti₉O₂₀ precursors. MgO–CaO–SiO₂–Al₂O₃ (MCAS) composite glass powder, fabricated by sol–gel method, is used as the low melting addition to lower the sintering temperatures of BaTi₄O₉ and Ba₂Ti₉O₂₀ dielectric. The addition of MCAS glass does not inhibit the residual satellite phases to transform into BaTi₄O₉ and Ba₂Ti₉O₂₀. For MCAS-doped BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics the major phases are BaTi₄O₉ and Ba₂Ti₉O₂₀, cordierite is observed as minor phase. The temperatures needed to densify the BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics are lowered down with the increase amount of MCAS glass addition. For BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics, both the densities and the dielectric constants (at 1 MHz) increase with the sintering temperature and decrease with the amount of MCAS glass addition. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: BaTi₄O₉; Ba₂Ti₉O₂₀; Calcination; Glass sintering aid; Sintering

1. Introduction

BaTi₄O₉ and Ba₂Ti₉O₂₀ were the two most common high-Q dielectric materials used in the microwave range. BaTi₄O₉ was first reported by Roy,¹ and Ba₂Ti₉O₂₀ by Jonker,² and they were investigated as microwave materials by O'Bryan and Plourde et al.^{3–6} The BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramic had superior dielectric properties for microwave resonator applications.^{4,5} For the preparation of monophasic samples of BaTi₄O₉ and Ba₂Ti₉O₂₀ from BaCO₃ and TiO₂ by conventional solid-state reaction, the stoichiometry must be precisely controlled, since there are various thermodynamically stable compounds in the vicinity of the desired composition of TiO₂-rich BaO–TiO₂ system: BaTi₃O₇, BaTi₄O₉, BaTi₅O₁₁, and Ba₄Ti₁₃O₃₀.^{3,4,7–9} In the study reported by Ritter et al., the pattern of BaO:TiO₂ = 1:4 was not completely formed BaTi₄O₉ until ≈1300°C.⁸ Lu et al. also reported that the BaO:TiO₂ = 2:9 powder, obtained by sol–gel method, must be calcined at 1200°C for 110 h to produce Ba₂Ti₉O₂₀ sole phase.⁷ In this

research, the solid-state reaction processes of BaCO₃ and TiO₂ to form BaTi₄O₉ and Ba₂Ti₉O₂₀ phase at different temperatures and times are developed, and our finding on the BaTi₄O₉ and Ba₂Ti₉O₂₀ compounds have shown some degree of difference from those in the literature.^{4–9}

In addition, a very high sintering temperature of ≈1400°C was required to achieve densification of the ceramics. For that, it is imperative to lower the sintering temperatures of the BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics in order to avoid the compositional fluctuation.^{3–6} Low melting glass additions, chemical processing, and smaller particle sizes of starting materials are three of the methods used to reduce the sintering temperature of dielectric.¹⁰ However, there are few references in the literature reporting the influence of glass addition on microwave properties of BaTi₄O₉ and Ba₂Ti₉O₂₀ dielectric.¹⁰ Because of these reasons, it drew our attention to, and provided motivation to study, the effects of glass flux on the sintering behavior and properties of BaTi₄O₉ and Ba₂Ti₉O₂₀ dielectric. MgO–CaO–SiO₂–Al₂O₃ (MCAS) composite glass,¹¹ which is fabricated by sol–gel method, is used as the low melting glass addition to lower the sintering temperature of BaTi₄O₉ and Ba₂Ti₉O₂₀ dielectric. The BaO:TiO₂ = 1:4 and

* Corresponding author.

BaO:TiO₂ = 2:9 powders used in this study do not form BaTi₄O₉ and Ba₂Ti₉O₂₀ completely, and the satellite phases of BaTi₄O₉ and Ba₂Ti₉O₂₀ are still residual in the using powders. It is found that the addition of MCAS glass does not inhibit the residual satellite phases to form the BaTi₄O₉ and Ba₂Ti₉O₂₀. Relationships among the sintering temperatures, phase formation, and the dielectric properties of MCAS-fluxed BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics are presented.

2. Experimental procedure

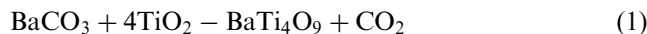
In the present investigation, a homogeneous glass of composition containing (in wt%) MgO5%, CaO19%, Al₂O₃26%, and SiO₂50% (abbreviated as MCAS) was prepared by the sol-gel method. In a typical laboratory scale synthesis using the nitrates, 40% colloidal silica was dispersed in 600 ml of deionized water, and concentrated nitric acid was also added into the solution. To this acidic suspension we added magnesium nitrate hexahydrate, calcium nitrate hexahydrate, and aluminum nitrate hexahydrate. The subsequent addition of ammonium hydroxide resulted in the quantitative precipitation of magnesium, calcium, and aluminum hydroxides. Then the glass powder was formed in the solide format. The solids were collected by filtration and calcined at 300°C for 1 h. The calcination step was desirable to convert any ammonium nitrate present to oxides of nitrogen and water. The resulting material was the MCAS glass precursor.

Proportionate amounts of reagent-grade starting materials of BaCO₃ and TiO₂ were mixed, according to the composition 2BaCO₃ + 9TiO₂ and BaCO₃ + 4TiO₂ and ball-milled for 5 h with deionized water. After drying, the reagent was ground with an agate mortar for 1 h. Then the powders were calcined at different temperatures and times. The crystal structures of calcined powders were examined by using an X-ray powder diffractometer. The Ba₂Ti₉O₂₀ precursor (calcined at 1200°C for 10 h) and BaTi₄O₉ precursor (calcined at 1150°C for 2 h) were mixed with 5 wt% or 10 wt% MCAS glass by ball milling with deionized water for 1 h. After drying, the powder was pressed into pellets uniaxially in a steel die. Typical dimensions of the pellets were 15mm in diameter and 1.5mm in thickness. Sintering of these Ba₂Ti₉O₂₀ pellets was carried out at a temperature between 1160 and 1360°C and BaTi₄O₉ pellets between 1150 and 1350°C under ambient conditions for a duration of 4 h. Crystallization of the sintered MCAS-Ba₂Ti₉O₂₀ and MCAS-BaTi₄O₉ ceramics were also investigated by X-ray diffraction patterns. Density of the sintered specimens as a function of sintering temperature was measured by the liquid displacement method using deionized water as a liquid (Archimedes method). After painting silver paste on both sides of the specimens

and fired at 700°C for about 20min, dielectric constants were measured with HP4192a impedance analyzer at 1 MHz.

3. Results and discussion

The X-ray diffraction patterns of calcined BaO:TiO₂ = 1:4 powders are shown in Fig. 1. Various phases were observed in BaO:TiO₂ = 1:4 oxide system. The conventional solid-state-reaction process for synthesizing BaTi₄O₉ compounds was commonly based on the following reaction:



However, the real solid reaction processes were usually more complex, and some satellite reactions might occur. Calcining at 1100°C for 2 h [Fig. 1(a)] the BaTi₄O₉ phase was formed, but the TiO₂ and satellite phases of BaTi₅O₁₁ and Ba₄Ti₁₃O₃₀ were also revealed. Proceeding calcination at 1150°C for 2 h [Fig. 1(b)] and 10 h [Fig. 1(c)] the BaTi₄O₉ was not the only phase, because the satellite phases of Ba₄Ti₁₃O₃₀ and BaTi₅O₁₁ were residual. Even though 1200°C and 10 h [Fig. 1(d)] were used as the calcining condition, the Ba₄Ti₁₃O₃₀ and BaTi₅O₁₁ phases were still residual. This suggests that the satellite phases of BaTi₅O₁₁ and Ba₄Ti₁₃O₃₀ are formed before the BaTi₄O₉ phase.

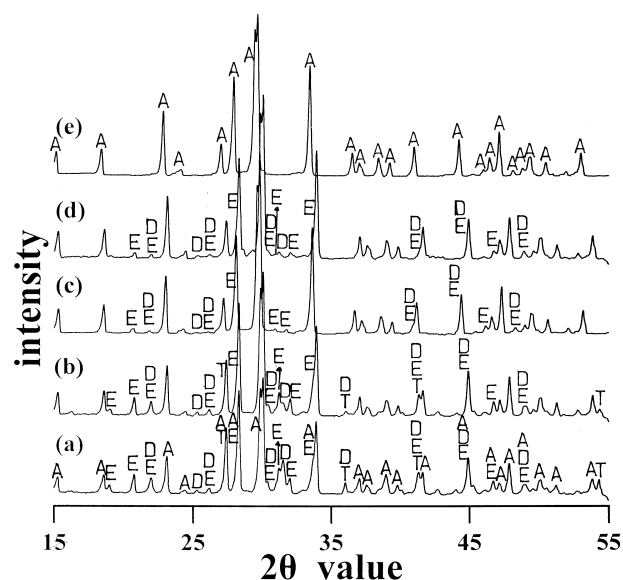
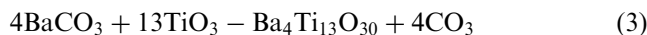
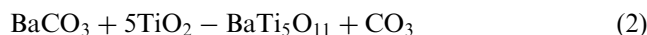
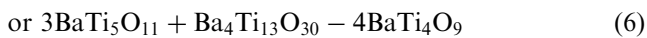
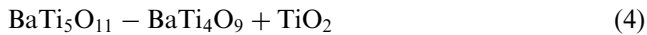


Fig. 1. The X-ray patterns of BaTi₄O₉ calcined powders (a) 1100°C for 2 h, (b) 1150°C for 2 h, (c) 1150°C for 10h, (d) 1200°C for 10 h, and (e) 1200°C for 70h (A: BaTi₄O₉, D:BaTi₅O₁₁, E: Ba₄Ti₁₃O₃₀, T:TiO₂).

Prolonging the calcining time at 1200°C for 70 h [Fig. 1(e)], only the BaTi₄O₉ was revealed. Ritter et al. reported that the BaO:TiO₂ = 1:4 revealed a two phase mixture of BaTi₂O₅ and BaTi₅O₁₁ at 700°C and a two phase mixture of Ba₄Ti₁₃O₃₀ and BaTi₅O₁₁ at 1000°C.⁸ Javadpour et al. reported the X-ray data obtained on the BaCO₃ + 4TiO₂ compound heated at 700°C for 4 h showed the presence of BaTi₅O₁₁ in addition to the lines for the BaTi₄O₉ phase.⁹ However, the small amount of BaTi₅O₁₁ phase observed by Raman spectroscopy was not detectable by X-ray powder diffraction experiments carried out on samples heated above 1000°C.⁹ Our finding on this compound showed some degree of difference from those reported by Ritter et al. and Javadpour et al.^{8,9} These reports and the results in this study suggest that reaction Eq. (1) and the following reaction may be processed together:



In this study, the powder calcined at 1150°C for 2 h was used as the initial BaTi₄O₉ powder. The X-ray diffraction patterns from the as-sintered surface of MCAS–BaTi₄O₉ ceramics as a function of sintering temperature and MCAS content are shown in Fig. 2. It has been reported that in the sintered MCAS glass existed the anorthite and cordierite as the two main crystalline structures.¹¹ As 0 wt%-MCAS-added BaTi₄O₉ ceramics was sintered at 1200°C [Fig. 2(a)] and 1300°C [Fig. 2(b)], the major phase was the BaTi₄O₉. For 5 and 10 wt%-MCAS-added BaTi₄O₉ ceramics and sintered at 1200°C, the major phase was BaTi₄O₉, and

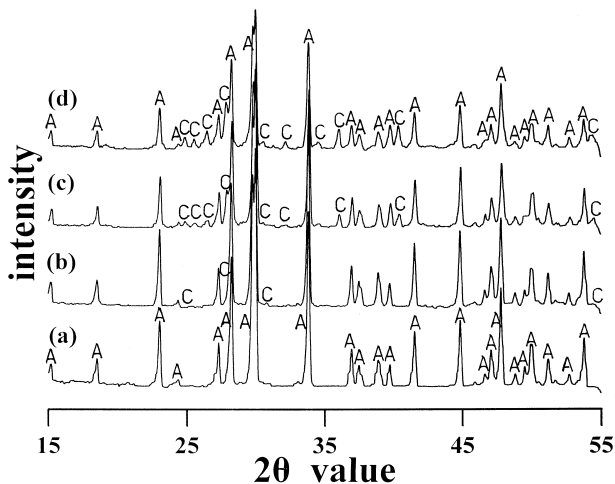
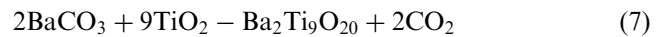


Fig. 2. The X-ray patterns of MCAS–BaTi₄O₉ dielectric for (a) 0 wt%, (c) 5 wt%, and (d) 10 wt% MCAS glass addition and sintered at 1200°C, (b) undoped and sintered at 1300°C. (C: cordierite, A: BaTi₄O₉, D: BaTi₅O₁₁, E:Ba₄Ti₁₃O₃₀).

the minor phase was cordierite [Fig. 2(c) and (d)]. The residual Ba₄Ti₁₃O₃₀ did not appear in the sintered MCAS–BaTi₄O₉ ceramics. These results suggest that MCAS does not inhibit the residual BaTi₅O₁₁ and Ba₄Ti₁₃O₃₀ to form BaTi₄O₉. Comparing Fig. 2(c) and (d), the diffraction intensity of cordierite increased and the diffraction intensity of BaTi₄O₉ decreased slightly as the amount of MCAS addition increased. These results also suggest that MCAS glass can really be used as a sintering aid of BaTi₄O₉ ceramics, because the MCAS glass improves the residual satellite phases to transform into BaTi₄O₉ phase.

The X-ray diffraction patterns of calcined Ba₂Ti₉O₂₀ powders are shown in Fig. 3. Furthermore, various phases were also observed in BaO–TiO₂ rare earth oxide system.^{7–9} The conventional solid-state-reaction process for synthesizing Ba₂Ti₉O₂₀ compounds were commonly based on the following reaction:



However, the real solid reaction processes are usually more complex, and some satellite reactions might also occur. As indicated in Fig. 3(a) (1150°C, 2 h) and Fig. 3(b) (1200°C, 2 h), at shorter calcining time BaTi₄O₉ is detected as the major phase, BaTi₅O₁₁ and TiO₂ as minor phases. At longer calcining time, as indicated in Fig. 3(c) (1150°C, 10 h) and Fig. 3(d) (1200°C, 10 h), the Ba₂Ti₉O₂₀ phase and satellite reaction phases of BaTi₄O₉ and BaTi₅O₁₁ coexist. This suggests that the BaTi₄O₉ and BaTi₅O₁₁ phases are formed before the Ba₂Ti₉O₂₀ phase.

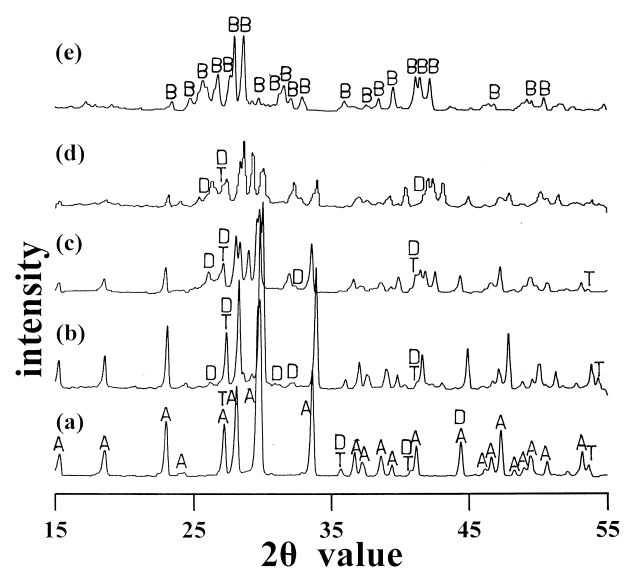
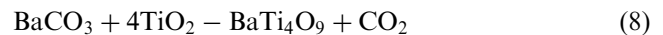
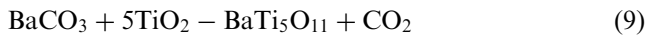
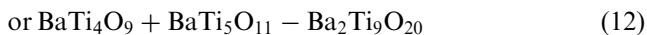
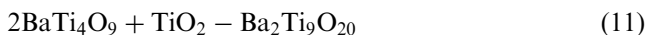


Fig. 3. The X-ray patterns of Ba₂Ti₉O₂₀ calcined powders (a) 1150°C for 2 h, (b) 1200°C for 2 h, (c) 1150°C for 10 h, (d) 1200°C for 10 h, and (e) 1200°C for 70 h (A: BaTi₄O₉, B: Ba₂Ti₉O₂₀, D: BaTi₅O₁₁, T:TiO₂).



O'Bryan and Thomson prepared $\text{BaTi}_5\text{O}_{11}$ as the major phase in a mixture of BaTi_4O_9 and rutile TiO_2 .¹² Ritter et al. reported that the synthesis of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ did not form until $\text{BaTi}_5\text{O}_{11}$ began to decompose.⁵ They also reported that if a mixture of barium and titanium species was hydrolyzed within 5 min after mixing, a precursor was produced which was disposed to form $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, $\text{BaTi}_5\text{O}_{11}$, and BaTi_4O_9 when heated to 1100°C ; prolonged heating can convert all of this material to $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. Javadpour and Eror found that at 1200°C , the Ba:Ti = 1:5 powders converted to $\text{BaTi}_5\text{O}_{11}$ and BaTi_4O_9 and only after extensive heat treatment at 1200°C were $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and TiO_2 produced.⁹ Ritter et al. also reported in their study of the controlled hydrolysis of alkoxide precursors that $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ did not begin to form until $\text{BaTi}_5\text{O}_{11}$ began to decompose.³ However, prolonged calcining time, as Fig. 3(e) (1200°C , 70 h) indicates, converts all of this material to $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. These reports and the results in this study suggest that the following reaction may be processed together:



In order to eliminate such satellite BaTi_4O_9 and $\text{BaTi}_5\text{O}_{11}$ phases from the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ calcination, a higher calcining temperature ($\geq 1200^\circ\text{C}$) and longer calcining time (≥ 10 h) were necessary. The calcining time was more important than the calcining temperature.

The X-ray diffraction patterns from the as-sintered surface of MCAS– $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics as a function of sintering temperature and MCAS content are shown in Fig. 4. In MCAS glass the anorthite and cordierite existed as the two main crystalline structures¹¹ and the used $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ precursor contained the satellite phases of $\text{BaTi}_5\text{O}_{11}$ and BaTi_4O_9 , therefore, phase control was expected to be extremely difficult in such a system. As undoped $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ precursor was sintered at 1260°C [Fig. 4(a)], the major phase was the $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and the $\text{BaTi}_5\text{O}_{11}$ phase is still residual. As 1340°C is used as the sintering temperature, the only crystalline phase is $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ [Fig. 4(b)]. The MCAS– $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ system prepared here was composed of one mainly crystalline phase, $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. Except $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ the cordierite was observed as minor phase [sintered at 1260°C , Fig. 4(c) and 4(d) for 5 wt% and 10 wt% MCAS addition, respectively]. Comparing Fig. 4(c) and 4(d), the diffraction intensity of cordierite increased and the diffraction intensity of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ decreased slightly as the amount of MCAS addition increased. As Fig. 4(a)–(d) shows, the satellite phases of BaTi_4O_9 and $\text{BaTi}_5\text{O}_{11}$ did not

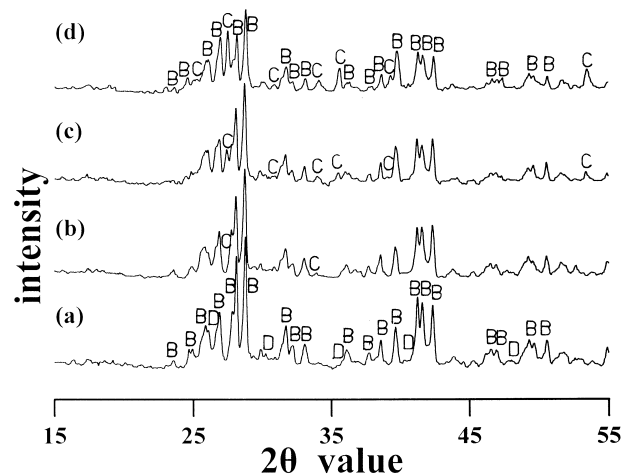


Fig. 4. The X-ray patterns of MCAS– $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ dielectric for (a) 0 wt%, (c) 5 wt%, and (d) 10 wt% MCAS glass addition and sintered at 1260°C , (b) 0 wt% MCAS addition and sintered at 1340°C (C: cordierite, A: BaTi_4O_9 , B: $\text{Ba}_2\text{Ti}_9\text{O}_{20}$, D: $\text{BaTi}_5\text{O}_{11}$).

appear in the undoped and MCAS-added $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics. These results suggest that MCAS glass does not inhibit the proceeding of reactions Eqs. (10)–(12).

The X-ray diffraction patterns showed that cordierite phase was independent to the BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ phase, the influences of MCAS glass on the lattice constant and dielectric constant of BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics were unavoidable. The lattice constants of undoped and MCAS-added BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ are shown in Fig. 5. and plotted versus the sintering temperature. The plot shows that the lattice parameters of the undoped BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics were almost unchanged with sintering temperature. The lattice parameters of BaTi_4O_9 ceramics were calculated to give the following values: $a = 1.453$ nm, $b = 0.380$ nm, and $c = 0.630$ nm, and the lattice parameters of $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics were calculated to give the following values: $a = 1.4815$ nm, $b = 1.4285$ nm, and $c = 0.7107$ nm. The MCAS-added BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics were isostructural with undoped BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics but had a slight difference in lattice parameters. The a and b parameters of MCAS-added BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics increase but c parameters slightly decreased with the sintering temperature and amount of MCAS glass addition.

SEM micrographs of MCAS– BaTi_4O_9 (sintering at 1200°C) and MCAS– $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics (sintering at 1260°C) are shown in Fig. 6. With no addition of MCAS glass, pores are easily observed in Fig. 6(a) for BaTi_4O_9 ceramics and Fig. 6(d) for $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics. As 5 and 10 wt% MCAS glass are added in BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics, the pores can be easily decreased. For both additive concentrations, the homogeneously fine microstructures, as shown in Fig. 6(b) and (c) for BaTi_4O_9 ceramics and Fig. 6(e) and (f) for $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics, almost no pores are observed.

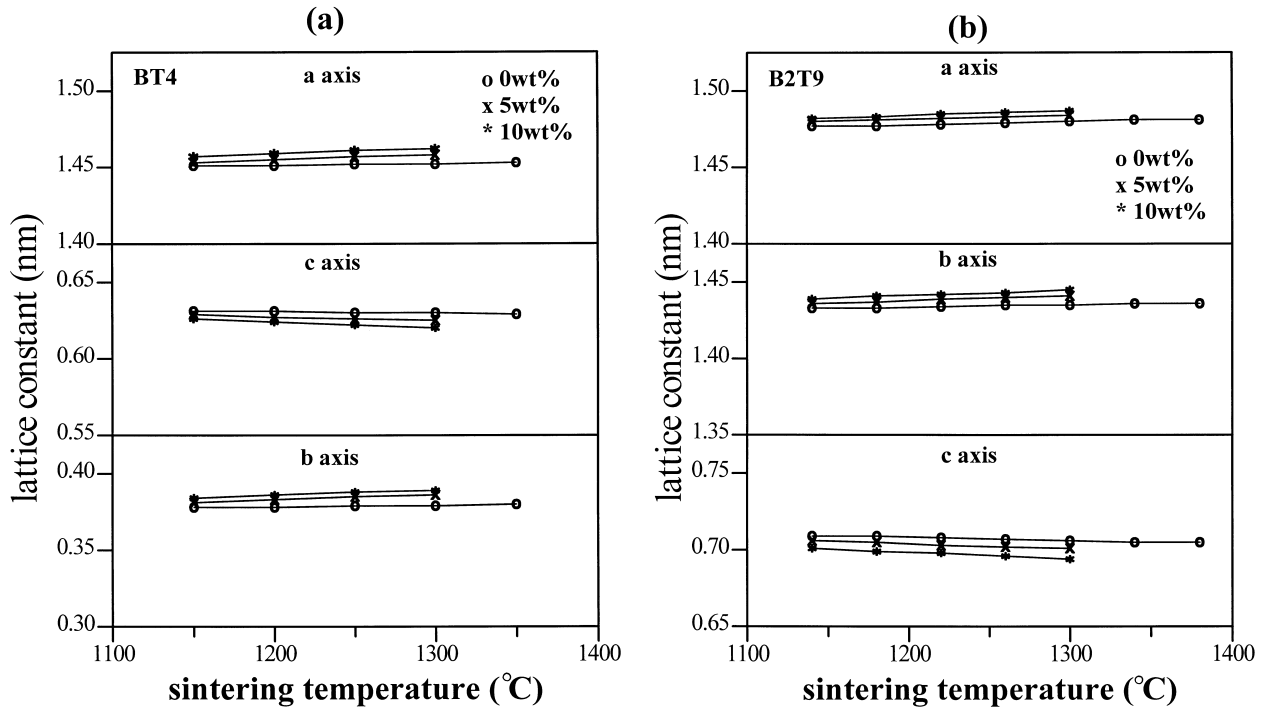


Fig. 5. Lattice constants of BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ as the functions of sintering temperatures and amount of MCAS glass addition (a) BaTi_4O_9 and (b) $\text{Ba}_2\text{Ti}_9\text{O}_{20}$.

The variation of the density of the BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics against the sintering temperature and glass content are shown in Table 1. As Table 1 shows, the densities of BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics increase with the increase of sintering temperature. The theoretical densities for the MCAS– BaTi_4O_9 and MCAS– $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics were calculated using Eq. (13):

$$D = (W_1 + W_2)/(W_1/D_1 + W_2/D_2) \quad (13)$$

where W_1 was the wt% of the BaTi_4O_9 or $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and W_2 was the wt% of MCAS glass, respectively; D_1 was the density of the BaTi_4O_9 or $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ and D_2 was the density of MCAS glass, respectively. In estimating the density of MCAS-added $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics, measured values for MCAS = 2.58 g/cm^3 ,¹¹ BaTi_4O_9 = 4.55 g/cm^3 ,¹³ and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ = 4.58 g/cm^3 were used. If the MCAS glass was continuous rather than dispersed in the BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics, Eq. (11) could be used to predict a composite density. The estimated theoretical densities were 4.390 and 4.255 g/cm^3 for 5 and 10 wt%-MCAS-added BaTi_4O_9 ceramics and were 4.417 and 4.278 g/cm^3 for 5 and 10 wt%-MCAS-added $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics. The temperatures for 0, 5, and 10 wt%-MCAS-added BaTi_4O_9 needed to reach >97% theoretical density were 1300, 1250, and 1200°C. The temperatures for 0, 5, and 10 wt%-MCAS-added $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ needed to reach >97% theoretical density were 1340, 1260, and 1220°C, respectively. The densities

showed that the ceramics samples were well sintered. The apparent densities of the sintered samples were about 98, 98.2, and 98.3% of the theoretical densities of 0, 5, and 10 wt%-MCAS-added $\text{Ba}_2\text{Ti}_9\text{O}_{20}$. This implies that BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics could be sintered at considerably lower temperature as MCAS glass was used as sintering agent.

The dielectric constants of MCAS-added BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics are measured at 1 MHz, and the results are shown in Fig. 6. For the same amount of MCAS addition, the dielectric constants increased with the increase of sintering temperature. It may be caused by the fact that the sintered densities increase with the sintering temperature. At 1 MHz, values of $K = 39.2$ and 37.8 were observed for undoped $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ (sintered at 1340 or 1380°C) and BaTi_4O_9 ceramics (sintered at 1300°C). Several investigators had studied the electrical properties of BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics,^{10,13} there was little variation for undoped BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics in the K values. The temperatures needed to obtain saturation dielectric constants were shifted to lower temperatures and the saturation values were decreased as the amount of MCAS glass increased. MCAS glass addition was found to have an effect on the dielectric constant. The dielectric constant of MCAS glass was measured to between 5.8 and 6.1 (at 1 MHz), the addition of MCAS glass will lower the dielectric constant of BaTi_4O_9 and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ ceramics. The reduction effects in dielectric constants are apparent in Fig. 6. At 1 MHz, dielectric constant decreased from

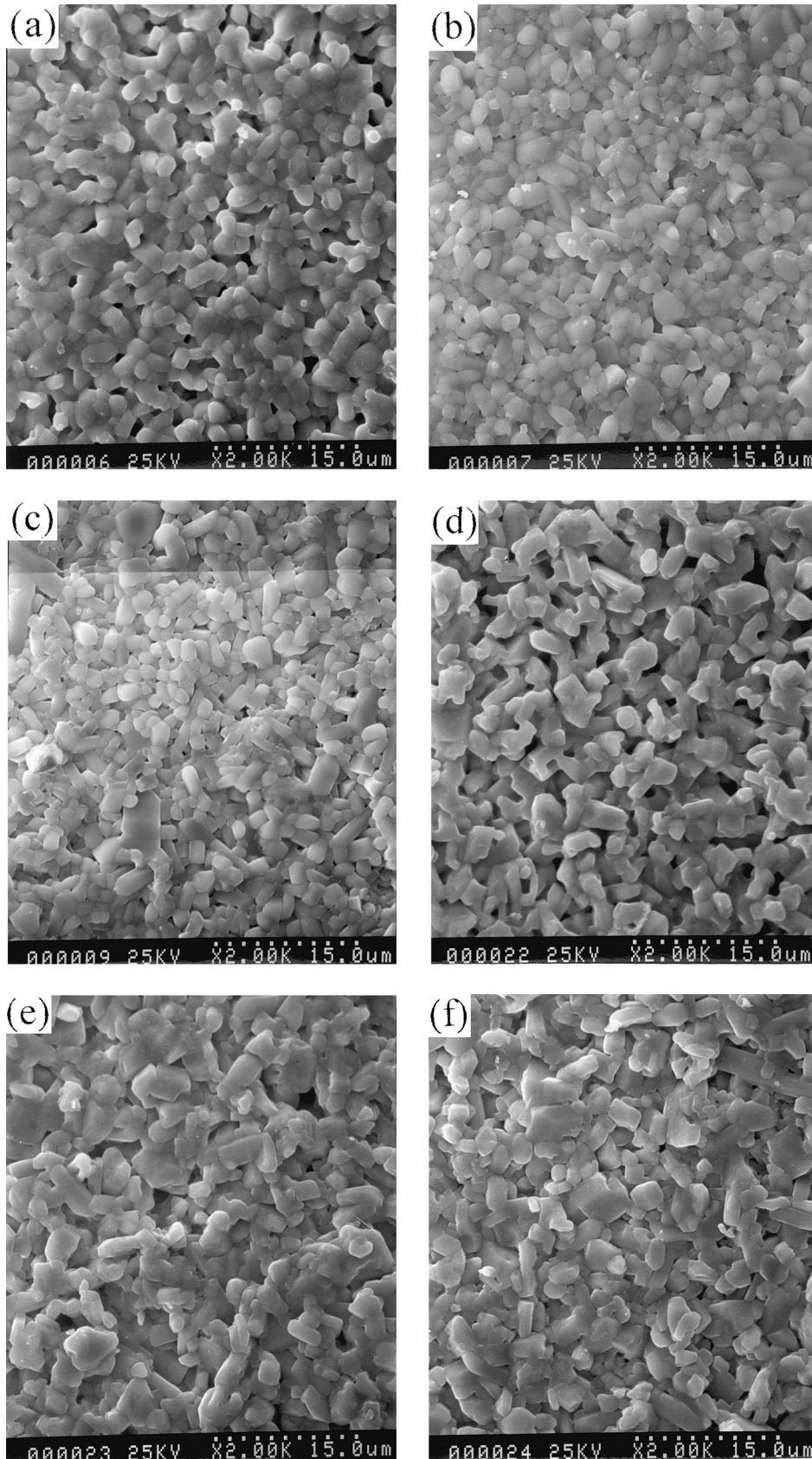


Fig. 6. The micrographs for BaTi_4O_9 sintered at 1200°C with (a) 0 wt%, (b) 5 wt%, and (c) 10 wt% MCAS glass added and for $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ sintered at 1260°C with (d) 0 wt%, (e) 5 wt%, and (f) 10 wt% MCAS glass added.

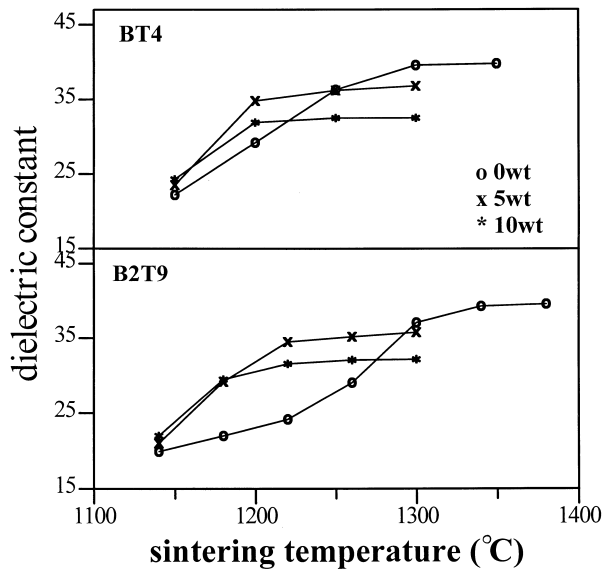


Fig. 7. The dielectric constants of MCAS–BaTi₄O₉ and MCAS–Ba₂Ti₉O₂₀ dielectrics as a function of sintering temperature (BT4: BaTi₄O₉, B2T9: Ba₂Ti₉O₂₀).

Table 1

The variation of the density of the BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics against the sintering temperature and glass content

	Composition/density (g/cm ³)		
	Undoped BaTi ₄ O ₉	BaTi ₄ O ₉ + 5 wt%	BaTi ₄ O ₉ + 10 wt%
Theoretical density	4.55	4.390	4.255
1150°C	2.652	3.028	3.283
1200°C	3.343	4.089	4.136
1250°C	4.092	4.263	4.169
1300°C	4.421	4.314	4.172
1350°C	4.468	–	–
	Undoped Ba ₂ Ti ₉ O ₂₀	Ba ₂ Ti ₉ O ₂₀ + 5 wt%	Ba ₂ Ti ₉ O ₂₀ + 10 wt%
Theoretical density	4.58	4.417	0.278
1140°C	2.243	2.571	2.638
1180°C	2.482	3.522	3.725
1220°C	2.897	4.182	4.164
1260°C	3.654	4.291	4.212
1300°C	4.343	4.341	4.214
1340°C	4.451	–	–
1380°C	4.495	–	–

about 39.2 for undoped Ba₂Ti₉O₂₀ dielectric to about 32.2 for Ba₂Ti₉O₂₀ ceramics with 10wt% MCAS glass added. The dielectric constant of densified MCAS–BaTi₄O₉ ceramics decreased from 37.8 for BaTi₄O₉

ceramics to 30.5 for 10wt%-MCAS-added BaTi₄O₉ ceramics.

4. Conclusions

The reaction process of BaO:TiO₂ = 1:4 and BaO:TiO₂ = 2:9 powders and the sintering characteristics of BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics with different amounts of MCAS glass addition have been developed in this study, and several conclusions are deduced as follows:

1. When BaO:TiO₂ = 1:4 at is calcined at 1150°C for 2 h and BaO:TiO₂ = 2:9 at 1200°C for 10h, the BaTi₄O₉ and Ba₂Ti₉O₂₀ are not formed completely, and the satellite phases are residual. The addition of MCAS composite glass does not inhibit the residual satellite phases to transform into BaTi₄O₉ or Ba₂Ti₉O₂₀.
2. The densities of MCAS–Ba₂Ti₉O₂₀ and MCAS–BaTi₄O₉ ceramics increase with sintering temperature but decrease with the amount of MCAS glass addition. The density curves shift to lower temperature as the amount of MCAS glass addition increases.
3. The dielectric constants of BaTi₄O₉ and Ba₂Ti₉O₂₀ ceramics increase with the sintering temperature and decrease with the increased amount of MCAS glass.

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