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Journal of the European Ceramic Society 27 (2007) 3027–3032
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Effect of dopants on synthesis of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ ceramics prepared by reaction-sintering process

Yi-Cheng Liou *, Ko-Hao Tseng, Tzu-Chin Chung

Department of Electronics Engineering, Kun-Shan University, Tainan Hsien, 71003 Taiwan, ROC

Available online 19 December 2006

Abstract

The effect of dopants on $BaTi_4O_9$ (BT4) and $Ba_2Ti_9O_{20}$ (B2T9) ceramics by the reaction-sintering process was investigated. CuO addition is more effective in lowering the sintering temperature of BT4 and B2T9 ceramics. MnO_2 and CuO addition are effective to obtain temperature stable BT4 ceramics. With MnO_2 addition, $Q \times f$ of BT4 ceramics could be raised. ZrO_2 addition is effective to obtain B2T9 ceramics with higher dielectric constant. With CuO addition, τ_f of B2T9 ceramics shifted toward negative values and 0 ppm/°C could be obtained. Optimum properties in BT4 doped with MnO_2 of $\varepsilon_r = 37.1$, $Q \times f = 51{,}200$ GHz (at 7 GHz) and $\tau_f = 0$ ppm/°C and in B2T9 doped with ZrO_2 of $\varepsilon_r = 37.9$, $Q \times f = 39{,}700$ GHz (at 7 GHz) and $\tau_f = 5.9$ ppm/°C were obtained.

Keywords: Dielectric properties; Reaction-sintering; Titanates

1. Introduction

Dielectric ceramics operated at microwave frequency have been widely investigated for the use of resonators and filters in the satellite and mobile communication systems. $BaTi_4O_9$ (BT4) ceramics were first reported by Rase and Roy[1] and $Ba_2Ti_9O_{20}$ (B2T9) ceramics were first investigated by Jonker and Kwestroo.[2] O'Bryan and Thomson found excellent microwave dielectric properties of these materials for resonator applications.[3] However, a very high sintering temperature >1300 °C is needed to obtain dense BT4 and B2T9 ceramics by conventional solid-state reaction process.[4–7] Yang et al. reported that lowered sintering temperature for dense BT4 and B2T9 was observed by adding MgO–CaO–SiO_2–Al_2O_3 (MCAS) glass powder.[5,6] Kim et al. obtained good microwave dielectric properties: $\varepsilon_r = 33$, $Q \times f = 27{,}000$ GHz at 9 GHz and $\tau_f = 7$ ppm/°C in BT4 ceramics with Zn–B–O glass addition after 900 °C/2 h sintering.[8] Huang et al. found B2T9 with 5 wt% B_2O_3 can be sintered to achieve 95% of theoretical density at 1200 °C and gives $\varepsilon_r = 36.5$ and $Q = 6700$ (at 6 GHz).[7] Chemical processes were also used to reduce the sintering temperature. Choy and Han[9] prepared BT4 ceramics of $\varepsilon_r \sim 36$, $Q \sim 4900$ at 10.3 GHz and $\tau_f \sim 16$ ppm/°C via citrate route at 1250 °C. Weng et al. produced BT4 ceramics of $\varepsilon_r = 35.6$, $Q \times f = 42{,}600$ GHz at 6 GHz and $\tau_f = 12$ ppm/°C by the polymeric precursor method and sintered at 1250 °C.[10] B2T9 ceramics were also investigated to lower the sintering temperature to 1200 °C by using the sol–gel process.[11]

Liou et al. reported a simple and effective reaction-sintering process in preparing $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT) and $Pb(Fe_{0.5}Nb_{0.5})O_3$ (PFN) ceramics.[12–17] These are the first successful synthesis of perovskite relaxor ferroelectric ceramics without any calcination involved. PMN ceramics with a density of 8.09 g/cm^3 (99.5% of the theoretical value) and high dielectric constant 19,900 (1 kHz) were obtained. This reaction-sintering process had also been used to produce other complex perovskite relaxor ceramics successfully. In the recent studies, we also prepared dense and pure phased $BaTi_4O_9$, $NiNb_2O_6$ and $CaNb_2O_6$ ceramics by this process successfully.[18–20] In this study, the effect of CuO, MnO_2 and ZrO_2 dopants on BT4 and B2T9 ceramics by the reaction-sintering process was investigated.

2. Experimental procedure

$BaTi_4O_9$ doped with 0.1 wt% MnO_2 (BT4M); 0.5 wt% CuO (BT4C) and $Ba_2Ti_9O_{20}$ doped with 0.2 wt% ZrO_2 (B2T9Z);

* Corresponding author. Tel.: +886 6 2050521; fax: +886 6 2050250.
E-mail address: ycliou@mail.ksu.edu.tw (Y.-C. Liou).

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doi:10.1016/j.jeurceramsoc.2006.11.039

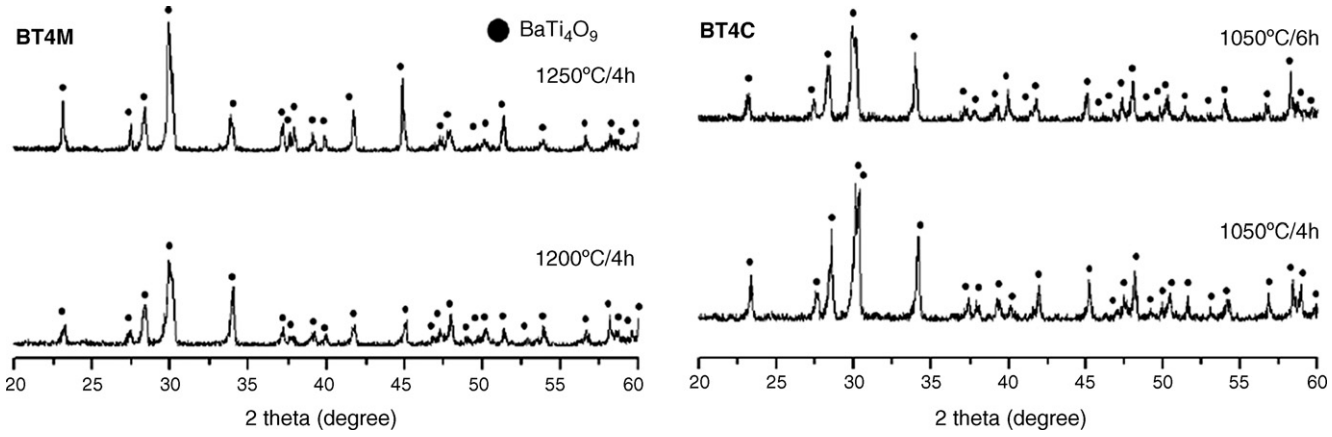

Fig. 1. XRD patterns of $BaTi_4O_9$ ceramics doped with 0.1 wt% MnO_2 and 0.5 wt% CuO.

0.5 wt% CuO (B2T9C) are compositions investigated. Reagent-grade carbonate and oxides $BaCO_3$ (99.8%), TiO_2 (99.9%), MnO_2 (99.9%), ZrO_2 (99.9%) and CuO (99%) were weighted and milled in acetone with zirconia balls for 12 h. After the slurry was dried and pulverized, the powder was pressed into pellets 12 mm in diameter and 1–2 mm thick (6–7 mm thick for microwave properties measurement). The pellets were then heated at a rate 10 °C/min and sintered in covered alumina cru-

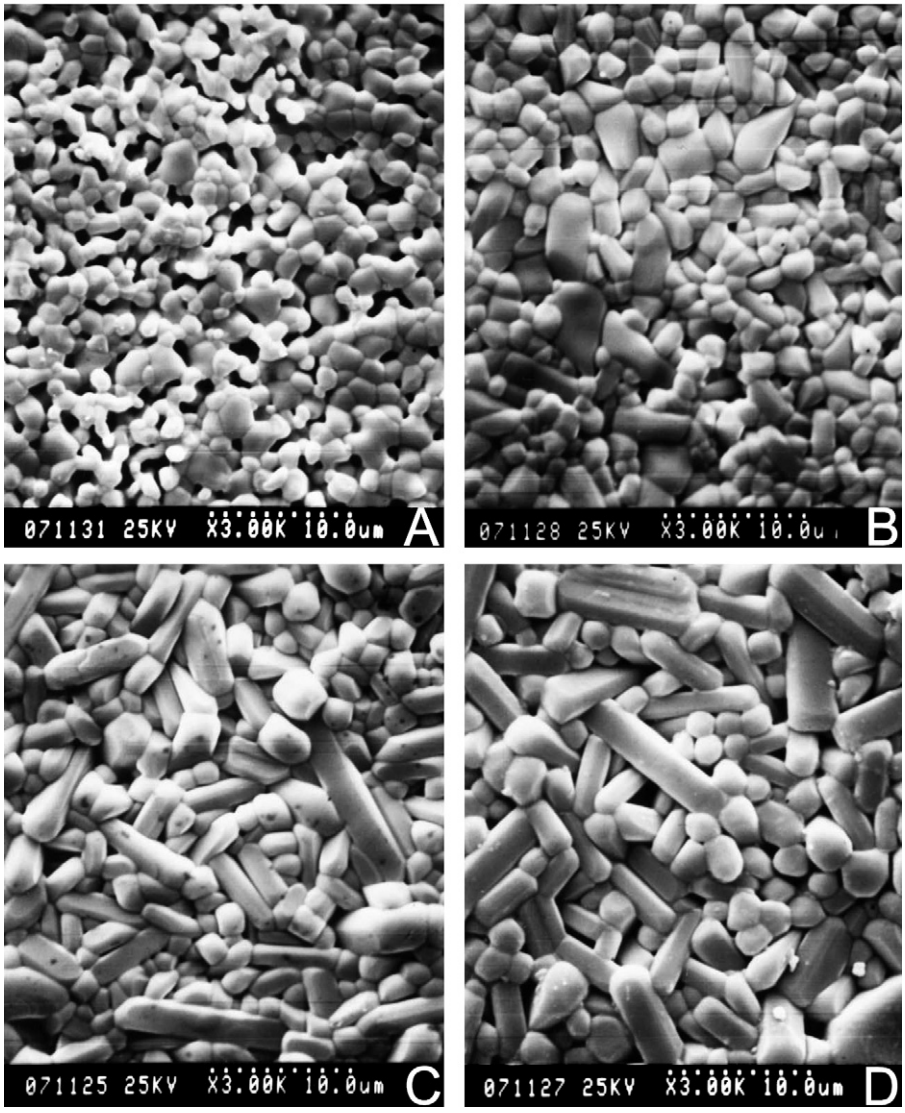

Fig. 2. SEM photos of $BaTi_4O_9$ ceramics doped with 0.1 wt% MnO_2 and sintered at (A) 1150 °C, (B) 1200 °C, (C) 1250 °C and (D) 1300 °C for 4 h.

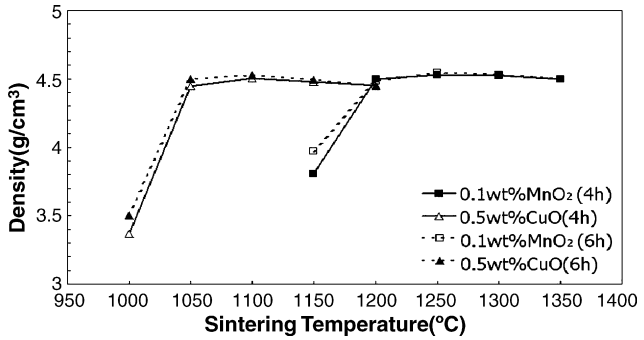

Fig. 3. Influence of sintering temperature and soak time on the density of $BaTi_4O_9$ ceramic doped with 0.1 wt% MnO_2 and 0.5 wt% CuO.

cible at temperatures ranging from 1000 to 1400 °C for 4 and 6 h in air.

The sintered pellets were analyzed by X-ray diffraction (XRD) to check the reflections of the phases. Microstructures were analyzed by scanning electron microscopy (SEM). The density of sintered pellets was measured by the water immersion method. The dielectric constants (ε_r) were calculated by the sizes of sample and the frequency of $TE_{0\,1\,1}$ mode using the Hakki–Coleman dielectric resonator method. [21] The temperature coefficient of resonant frequency (τ_f) at microwave frequency was measured in the temperature range from 25 to 85 °C, and calculated by the following equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \times 10^6 \,(\text{ppm}/^\circ\text{C})$$

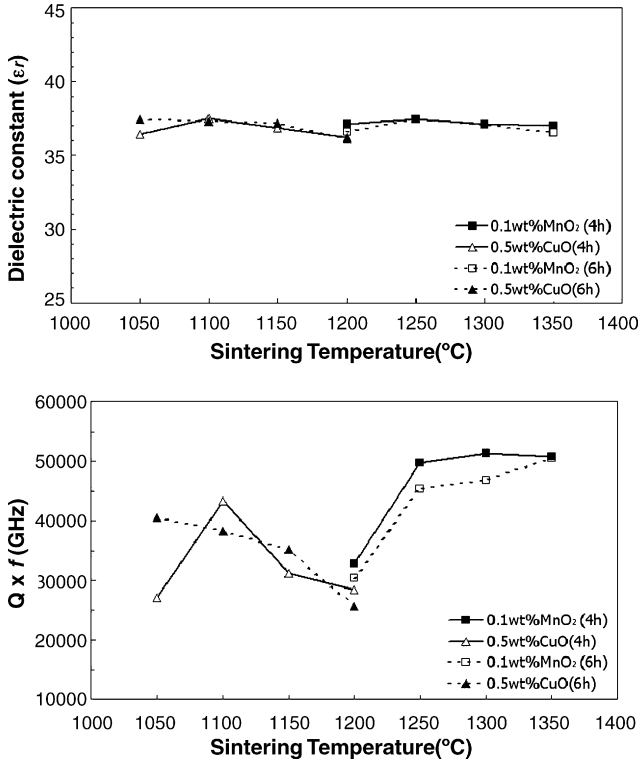

Fig. 4. ε_r and $Q \times f$ of $BaTi_4O_9$ ceramics doped with 0.1 wt% MnO_2 and 0.5 wt% CuO.

where f_{85} and f_{25} are $TE_{0\,1\,\delta}$ resonant frequency at 85 and 25 °C, respectively. N5230A network analyzer (Agilent) was employed in the measurement.

3. Results and discussions

The XRD patterns of sintered BT4M and BT4C ceramics are shown in Fig. 1. It can be seen that all the reflections match with those of BT4 phase in ICDD PDF # 340070. Weng et al. proposed that BT4 phase associated with $Ba_4Ti_{13}O_{30}$ and B2T9 phases were obtained after sintered at 1250 °C for 3 h by the conventional mixed oxide method. B2T9 phase is still detected even after 3 h sintering at 1300 °C.[10] Xu et al. reported that a mixture of BT4, $Ba_4Ti_{13}O_{30}$ and B2T9 phases were observed in the 1100 °C/4 h heated BT4 precursor prepared by a sol–gel method using EDTA as a chelating agent. Single phase BT4 cannot be synthesized even after heating the precursors for 2 h at 1200 °C. B2T9 phase was still detected.[22] Therefore reaction-sintering process can efficiently transform the mixture of $BaCO_3$ and TiO_2 into BT4 phase even the calcination stage is bypassed. SEM photos of BT4M ceramics sintered at 1150–1300 °C for 4 h are illustrated in Fig. 2. An 1150 °C is not high enough for the densification and pores can be easily found. Dense pellets

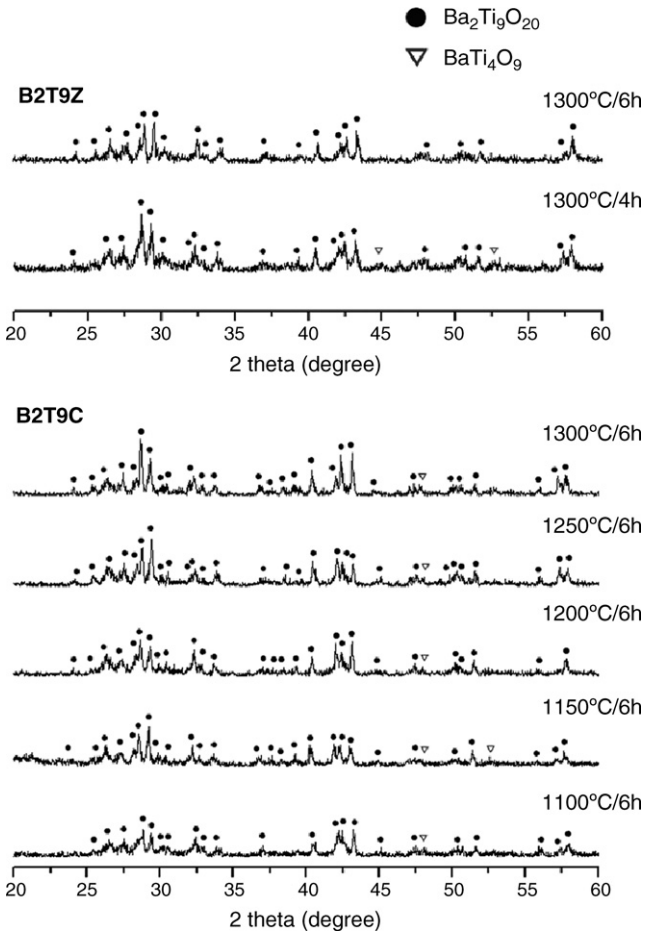

Fig. 5. XRD patterns of $Ba_2Ti_9O_{20}$ ceramics doped with 0.2 wt% ZrO_2 and 0.5 wt% CuO.

could be obtained at sintering temperatures above 1200 °C. At 1250 and 1300 °C, rod grains were formed. This is the same as in BT4 ceramics prepared by the reaction-sintering process.[18] Influence of sintering temperature and soak time on the density of BT4M and BT4C ceramics is shown in Fig. 3. Density saturated at temperatures above 1200 and 1050 °C in BT4M and BT4C, respectively. High sintered density >98% of theoretical value 4.55 g/cm^3 could be obtained. This proves highly dense BT4M and BT4C ceramics can be prepared by reaction-sintering process easily even without the calcining stage. In our previous study, a maximum density 4.45 g/cm^3 was found in BT4 ceramics sintered at 1200 °C.[18] Also from Fig. 3, CuO addition is more effective in lowering the sintering temperature of BT4 ceramics. Lu et al. obtained a maximum density about 97% of theoretical value in BT4 ceramics with ZnO–B_2O_3 glass phase after 1100 °C/2 h calcining and 1250 °C/2 h sintering by the conventional mixed oxide method.[23]

Fig. 4 shows ε_r and $Q \times f$ of BT4M and BT4C ceramics sintered at various temperatures and soak time. ε_r in a range 36.5–37.5 and $Q \times f$ of 30,400–51,200 GHz (at 7 GHz) were obtained in BT4M. While in BT4C, ε_r of 36.1–37.5 and $Q \times f$ of 25,500–43,200 GHz (at 7 GHz) were found. The temperature coefficient of resonant frequency τ_f of all BT4M and BT4C ceramics are 0 ppm/°C. In BT4 ceramics prepared by the reaction-sintering process, $\varepsilon_r = 37$–38, $Q \times f = 34{,}200$–$44{,}600$ GHz (at 7 GHz) and $\tau_f = 4$–6 ppm/°C were found after 2–6 h sintering at 1200–1280 °C. It implies MnO_2 and CuO addition are effective to obtain temperature stable BT4 ceramics. With MnO_2 addition, $Q \times f$ of BT4 ceramics could be raised. Optimum property was obtained in BT4M of $\varepsilon_r = 37.1$, $Q \times f = 51{,}200$ GHz (at 7 GHz) and $\tau_f = 0$ ppm/°C after 4 h sintering at 1300 °C.

The XRD patterns of sintered B2T9Z and B2T9C ceramics are shown in Fig. 5. It can be seen the reflections match with those of ICDD PDF # 350051 for B2T9. Therefore, reaction-sintering process can efficiently transform the mixture of $BaCO_3$ and TiO_2 into B2T9 phase. Minor BT4 phase appeared in these pellets except B2T9Z at 1300 °C/6 h sintering. ZrO_2 addition is

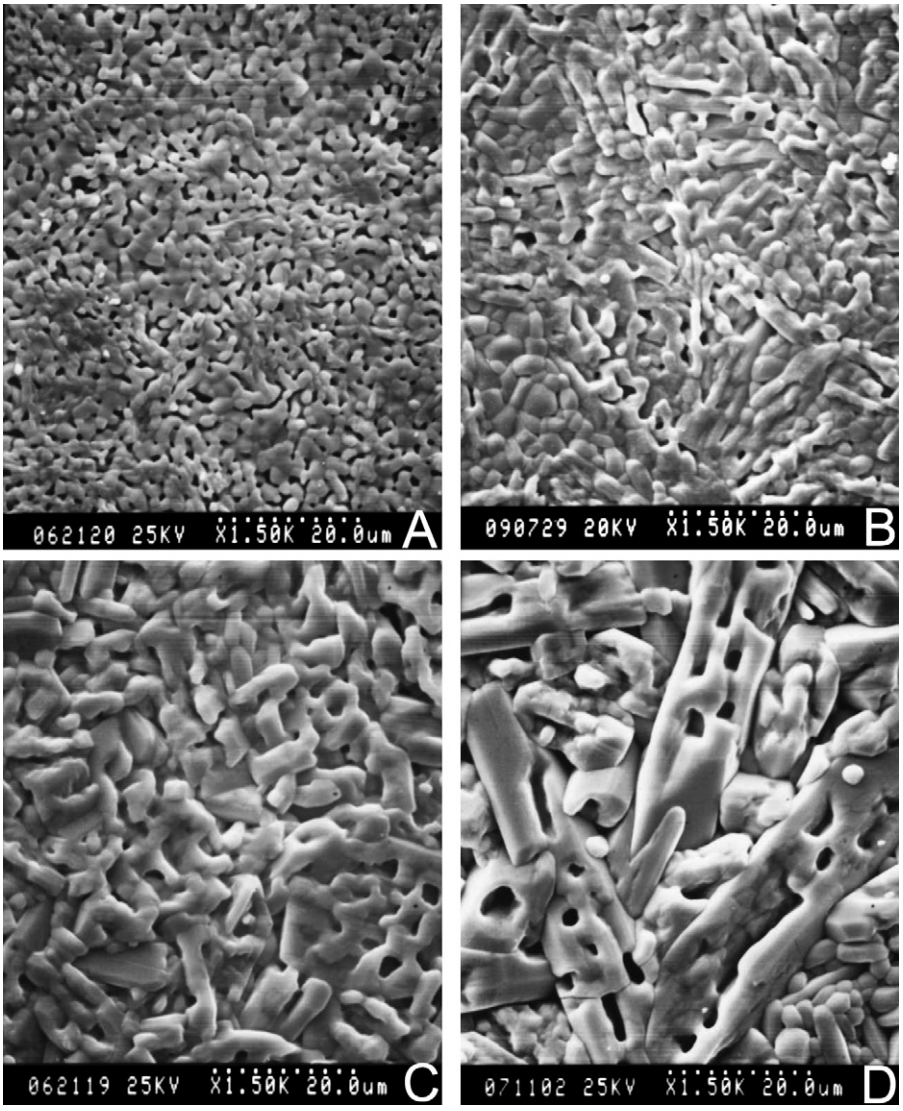

Fig. 6. SEM photos of $Ba_2Ti_9O_{20}$ ceramics doped with 0.2 wt% ZrO_2 and sintered at (A) 1200 °C, (B) 1250 °C, (C) 1300 °C and (D) 1350 °C for 4 h.

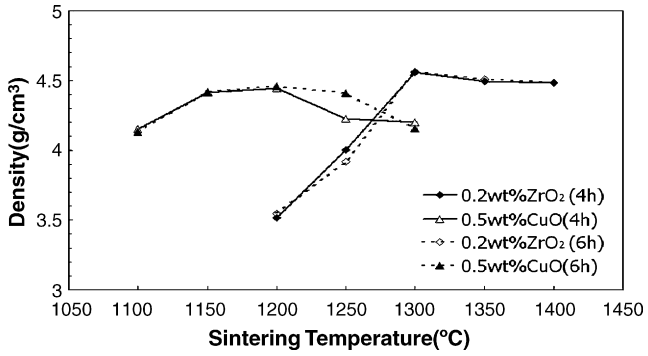

Fig. 7. Influence of sintering temperature and soak time on the density of $Ba_2Ti_9O_{20}$ ceramic doped with 0.2 wt% ZrO_2 and 0.5 wt% CuO.

more effective in obtaining pure B2T9 ceramics. BT4 phase was often observed in forming B2T9 by the solid-state reaction. Fang et al. reported that BT4 phase appeared in the calcined mixture of $BaCO_3$ and TiO_2 at temperatures between 900–1200 °C. B2T9 phase appeared after 3 h calcined at 1200 °C but could not be completely formed even after calcined for 12 h.[24] While in the investigation of Yang et al., $BaTi_5O_{11}$ and TiO_2 minor phases were formed along with BT4 major phase in the calcined mixture of $BaCO_3$ and TiO_2 at 1150–1200 °C for 2 h. B2T9 phase completely formed after calcined at 1200 °C for 70 h.[6] SEM photos of B2T9Z ceramics sintered at 1200–1350 °C for 4 h are illustrated in Fig. 6. A 1200 °C is not high enough for the densification and pores can be easily found. Dense pellets could be obtained at sintering temperatures above 1250 °C and the morphology of grains is similar to B2T9 ceramics prepared by the reaction-sintering process. The influence of sintering temperature and soak time on the density of B2T9Z and B2T9C ceramics is shown in Fig. 7. Density saturated at temperatures above 1300 and 1150 °C in B2T9Z and B2T9C, respectively. High sintered density >98% of theoretical value 4.577 g/cm^3 could be obtained in B2T9Z and a maximum 4.56 g/cm^3 appeared at 1300 °C. Lower density is observed in B2T9C. Also from Fig. 7, CuO addition is more effective in lowering the sintering temperature of B2T9 ceramics. Huang et al. obtained a maximum density 4.42 g/cm^3 after 1200 °C/3 h calcined and 1380 °C/3 h sintered.[7] Yang and co-workers obtained a highest density 4.495 g/cm^3 after 1200 °C/10 h calcining and 1380 °C/4 h sintering.[6] Wang et al. obtained a density 4.55 g/cm^3 in B2T9 ceramics with 4 wt% ZrO_2 added after 1300 °C/4 h sintered.[25] Therefore, reaction-sintering process is a simple and effective method to produce highly dense B2T9 ceramics.

Fig. 8 shows ε_r and $Q \times f$ of B2T9Z and B2T9C ceramics sintered at various temperatures and soak time. $\varepsilon_r = 25.8$–40.7, $Q \times f = 25{,}400$–$40{,}300$ GHz (at 7 GHz) and $\tau_f = 2.8$–12.1 ppm/°C were obtained in B2T9Z. While in B2T9C, $\varepsilon_r = 31$–34.5, $Q \times f = 13{,}900$–$27{,}300$ GHz (at 7 GHz) and $\tau_f = -8.5$ to 0 ppm/°C were found. In B2T9 ceramics prepared by the reaction-sintering process, $\varepsilon_r = 36$–38, $Q \times f = 25{,}500$–$41{,}300$ GHz (at 7 GHz) and $\tau_f = 0$–11.8 ppm/°C were found after 4 and 6 h sintering at 1280–1350 °C. It implies ZrO_2 addition is effective to obtain B2T9 ceramics with higher dielectric constant. With CuO addition, τ_f of B2T9 ceramics shifted toward negative values and 0 ppm/°C could be obtained. Optimum property was obtained in B2T9Z of $\varepsilon_r = 37.9$, $Q \times f = 39{,}700$ GHz (at 7 GHz) and $\tau_f = 5.9$ ppm/°C after 4 h sintering at 1300 °C.

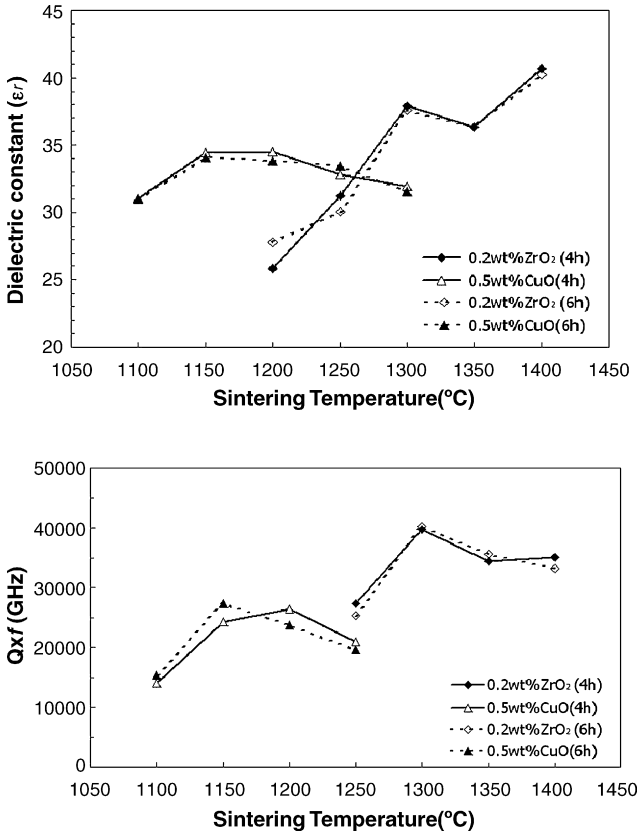

Fig. 8. ε_r and $Q \times f$ of $Ba_2Ti_9O_{20}$ ceramics doped with 0.2 wt% ZrO_2 and 0.5 wt% CuO.

4. Conclusions

Pure $BaTi_4O_9$ phase were obtained successfully by a reaction-sintering process in $BaTi_4O_9$ doped with MnO_2 and CuO. High sintered density >98% of theoretical value 4.55 g/cm^3 could be obtained. CuO addition is more effective in lowering the sintering temperature of $BaTi_4O_9$ ceramics. MnO_2 and CuO addition are effective to obtain temperature stable $BaTi_4O_9$ ceramics. With MnO_2 addition, $Q \times f$ of $BaTi_4O_9$ ceramics could be raised. Optimum property was obtained in BT4M of $\varepsilon_r = 37.1$, $Q \times f = 51{,}200$ GHz (at 7 GHz) and $\tau_f = 0$ ppm/°C after 4 h sintering at 1300 °C.

Minor $BaTi_4O_9$ phase appeared in B2T9Z and B2T9C ceramics except B2T9Z at 1300 °C/6 h sintering. High sintered density >98% of theoretical value 4.577 g/cm^3 could be obtained in B2T9Z and a maximum 4.56 g/cm^3 appeared at 1300 °C. Lower density is observed in B2T9C. CuO addition is more effective in lowering the sintering temperature of $Ba_2Ti_9O_{20}$ ceramics. ZrO_2 addition is effective to obtain B2T9 ceramics with higher dielectric constant. With CuO addition, τ_f of B2T9 ceramics shifted toward negative values and 0 ppm/°C could be obtained. Optimum property was obtained in B2T9Z of $\varepsilon_r = 37.9$,

$Q \times f = 39{,}700$ GHz (at 7 GHz) and $\tau_f = 5.9$ ppm/°C after 4 h sintering at 1300 °C.

Acknowledgements

The authors are grateful to Miss Shi-Yuea Hsu for her help in obtaining the SEM photos. This study was supported by the National Science Council of the Republic of China under contract NSC 94-2216-E-168-002.

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