Journal of Alloys and Compounds 509 (2011) 6884–6888

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Low temperature sintering and microwave dielectric properties of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics with $BaCu(B_2O_5)$ additions

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ARTICLE INFO

Article history:
Received 15 December 2010
Received in revised form 21 March 2011
Accepted 30 March 2011
Available online 6 April 2011

Keywords:
$(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$
Microwave dielectric properties

ABSTRACT

The effects of $BaCu(B_2O_5)$ additives on the sintering temperature and microwave dielectric properties of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics were investigated. The $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics were not able to be sintered below 1000 °C. However, when $BaCu(B_2O_5)$ were added, they were sintered below 1000 °C and had the good microwave dielectric properties. It was suggested that a liquid phase with the composition of $BaCu(B_2O_5)$ was formed during the sintering and assisted the densification of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics at low temperature. $BaCu(B_2O_5)$ powders were produced and used to reduce the sintering temperature of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics. Good microwave dielectric properties of $Q \times f = 35{,}000$ GHz, $\varepsilon_r = 18.5.0$ and $\tau_f = -51$ ppm/°C were obtained for the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics containing 7 wt.% mol% $BaCu(B_2O_5)$ sintered at 950 °C for 4 h.

1. Introduction

Recently, low temperature co-fired ceramic (LTCC) multilayer devices, composed of alternating dielectric ceramics and internal metallic electrode layers, have been extensively investigated for the miniaturization of microwave dielectric components [1–3]. LTCC multilayer devices consist of alternating microwave dielectric ceramics and internal metallic electrode layers. Ag has been widely used as the metallic electrode, because of its high conductivity and low cost. However, the melting temperature of Ag is low, about 961 °C, whereas the sintering temperature of the microwave dielectric ceramics is generally above 1400 °C. Therefore, for the fabrication of multilayer devices, it is necessary to develop microwave dielectric ceramics with a low sintering temperature, which can be co-fired with Ag.

$MgTiO_3$-based ceramics, which have low dielectric loss, have been intensively studied for years. $MgTiO_3$–$CaTiO_3$ ceramics made of a mixture of modified α-Al_2O_3 structured magnesium titanate ($MgTiO_3$: $\varepsilon_r \sim 17$, $Q \times f \sim 160{,}000$ (at 9 GHz), and $\tau_f \sim -50$ ppm/°C) [4] and perovskite structured calcium titanate ($CaTiO_3$: $\varepsilon_r \sim 170$, $Q \times f \sim 3600$ (at 7 GHz), and $\tau_f \sim 800$ ppm/°C) [5] have been applied in dielectric resonators and patch antennas. With a ratio of Mg:Ca = 95:5, 0.95 $MgTiO_3$–0.05 $CaTiO_3$ ceramic has an $\varepsilon_r \sim 21$, a $Q \times f \sim 56{,}000$ (at 7 GHz), and a zero τ_f value [4]. However, it requires sintering temperatures as high as 1400–1450 °C. For practical applications, their sintering temperature needs to be reduced [6–9]. Since the ionic radius of Zn^{2+} (0.083 nm) is similar to that of Mg^{2+} (0.078 nm), Mg^{2+} ions can be substituted by Zn^{2+} ions to form (Mg, Zn)TiO_3 compositions. Heavily Zn-substituted $MgTiO_3$, which leads to the formation of (Mg, Zn)TiO_3 solid solution, has been shown to have a relatively low sintering temperature. For example, when sintered at 1200 °C, $(Mg_{0.7}Zn_{0.3})TiO_3$ has an $\varepsilon_r \sim 19.8$, a $Q \times f \sim 142{,}000$ GHz, and $\tau_f \sim -66$ ppm/°C [10]. With the partial replacement ($Mg_{0.7}Zn_{0.3}$) by Co, $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ had excellent dielectric properties with an $\varepsilon_r \sim 20$, $Q \times f \sim 163{,}560$ GHz, and a $\tau_f \sim -65$ ppm/°C after being sintered at a low sintering temperature of 1200 °C [10].

Recently, a small amount of B_2O_3 and CuO additives were used to reduce the sintering temperature of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics. They were well sintered at 870 °C and had good microwave dielectric properties. $BaCu(B_2O_5)$ second phase was observed in the B_2O_3 and CuO added specimens and it was assumed to exist as a liquid phase and assist in the densification of the ceramics at low temperature. According to a previous work, $BaCu(B_2O_5)$ phase was formed at 700 °C and melted above 850 °C [11]. Moreover, the $BaCu(B_2O_5)$ ceramic sintered at 810 °C had a dielectric constant (ε_r) of 7.4, a quality factor ($Q \times f$) of 50,000 GHz and a temperature coefficient of resonance frequency (τ_f) of −32 ppm/°C. Since the $BaCu(B_2O_5)$ ceramic had a low melting temperature and good microwave dielectric properties, it could be used as a low temperature sintering aid in the microwave dielectric materials used for LTCC application. In this work, $BaCu(B_2O_5)$(BCB) ceramic powder was added to $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics to reduce their sintering temperature and the effect of BCB addition on their microwave dielectric properties was studied.

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doi:10.1016/j.jallcom.2011.03.172

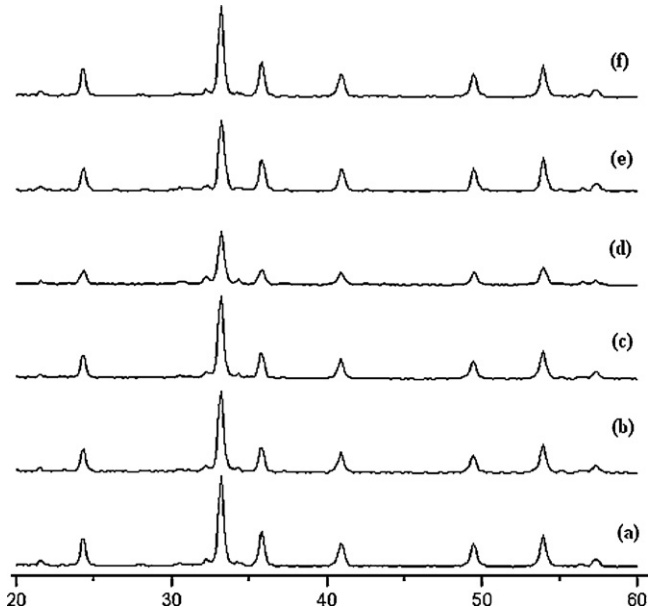


Fig. 1. X-ray diffraction patterns of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ with 5 wt.% $BaCu(B_2O_5)$ additions sintered at various temperatures for 4 h.

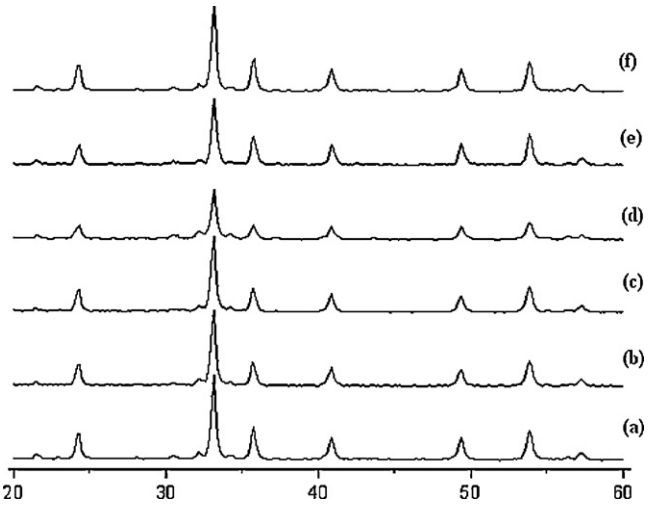


Fig. 2. X-ray diffraction patterns of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ with 7 wt.% $BaCu(B_2O_5)$ additions sintered at various temperatures for 4 h.

2. Experimental procedures

To prepare the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics, MgO, ZnO, CoO and TiO_2 were mixed in a nylon jar with zirconia balls for 24 h, and then dried and calcined at 900 °C for 4 h. All chemicals have purity better than 99%, all supplied by High Purity Chemicals, Japan. To synthesize the BCB ceramic powder, $BaCO_3$ (>99%), CuO (>99%) and B_2O_3 (>99%) were mixed for 4 h in a nylon jar with zirconia balls, then dried and calcined at 700 °C for 3 h. After subsequent ball-milling with 5–7.0 wt.% BCB, the powders were uniaxially pressed into disks of 11 mmin diameter and 5.5 mm in thickness under the pressure of about 150 MPa. The $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ samples were sintered at 900–1025 °C for 4 h in air doped with BCB.

The crystalline phases of the calcined powder and the sintered ceramics were identified by X-ray diffraction pattern analysis. The microstructure observations and analysis of sintered surface were performed using a scanning electron microscope (SEM, Philips XL-40FEG). Energy dispersive spectroscopy (EDX) was used to identify the existence of second phases. The bulk densities of the sintered pellets were measured using the Archimedes method. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman [12] dielectric resonator method under TE011 and TE01σ modes as modified and improved by Courtney [13]. The dielectric resonator was positioned between two brass plates. A system comprising of an HP8757D network analyzer and an HP8350B sweep oscillator was employed in the measurement. An identical technique was applied in measuring the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from +25 °C to +80 °C. The τ_f value (ppm/°C) can be calculated by noting the change in resonant frequency (Δf):

$$\tau_f = \frac{f2 - f1}{f1(T2 - T1)}$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramic with 5 wt.% BCB sintered at various temperatures for 4 h. The XRD patterns showed that peaks indicating the presence of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main crystalline phase. It is understood that crystal structures of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ rhombohedral (ICDD-PDF #01-073-7752). According to the XRD patterns, the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ phase exists in these specimens. X-ray diffraction patterns of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics system have not been changed significantly with sintering temperatures in the range 900–1025 °C. The XRD patterns show peaks indicating the presence of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ as the main crystalline phase. The liquid phase was found at the grain boundary of the specimen. Therefore, the densification of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics at low temperatures was attributed to the presence of the liquid phase. Furthermore, since the BCB phase starts to melt at approximately 850 °C, the liquid phase is considered to have a composition similar to the BCB. According to a previous work, liquid phase was also observed in the BCB-added $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics without second phase. Figs. 1 and 2 show that the phases and peak intensity remained almost unchanged with the addition of BCB up to 7 wt.% and sintering temperature up to 1025 °C.

SEM micrographs of 7 wt.% BCB doped $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ samples sintered at different sintering temperatures (900 °C, 925 °C, 950 °C, 975 °C, 1000 °C and 1025 °C) are shown in Fig. 3. It can be seen that the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics were not dense and the grain did not grow at 900 °C as shown in Fig. 3(a). However, rapid grain growth was observed at 950 °C in Fig. 3(c) and the pores were almost eliminated for specimen sintered at 950 °C in Fig. 3(c). Therefore, it can be deduced that the low densities of the compounds are resulted from the porous specimens sintered at 900 °C or 925 °C, and that the densities of samples increase with increasing sintering temperature are shown in Fig. 3. Fig. 3(a)–(e) due to the liquid-phase effect, which indicated that BCB additive has successfully acted as sintering aid for a liquid-phase sintering to enhance the sintering ability of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramic. These may directly affect the microwave dielectric properties of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ compounds.

The energy dispersive X-ray (EDX) analysis was used in combination with scanning electron microscopy to distinguish every grain for $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramic with 7 wt.% sintered at 950 °C, as shown in Fig. 4(a). The EDX datum and data of corresponding spots A–B are shown in Fig. 4(b), respectively. The grain morphology of well developed $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics could be grouped into one types: both large grains (spot A), indicating Mg–Ti phase, were $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$, and small cubic-shape grains (spot B) were still $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$. The EDX evidences are in agreement with the XRD results obtained from $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics.

Fig. 5 shows the bulk densities of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics sintered at various temperatures for 4 h. With increasing temperature, the bulk density increased to a maximum value of 3.79 g/cm^3 at 950 °C, and then it decreased. The reduction of density due to the abnormal grain growth is shown in Fig. 3. The variation of ε_r was consistent with that of density. The dielectric constant also

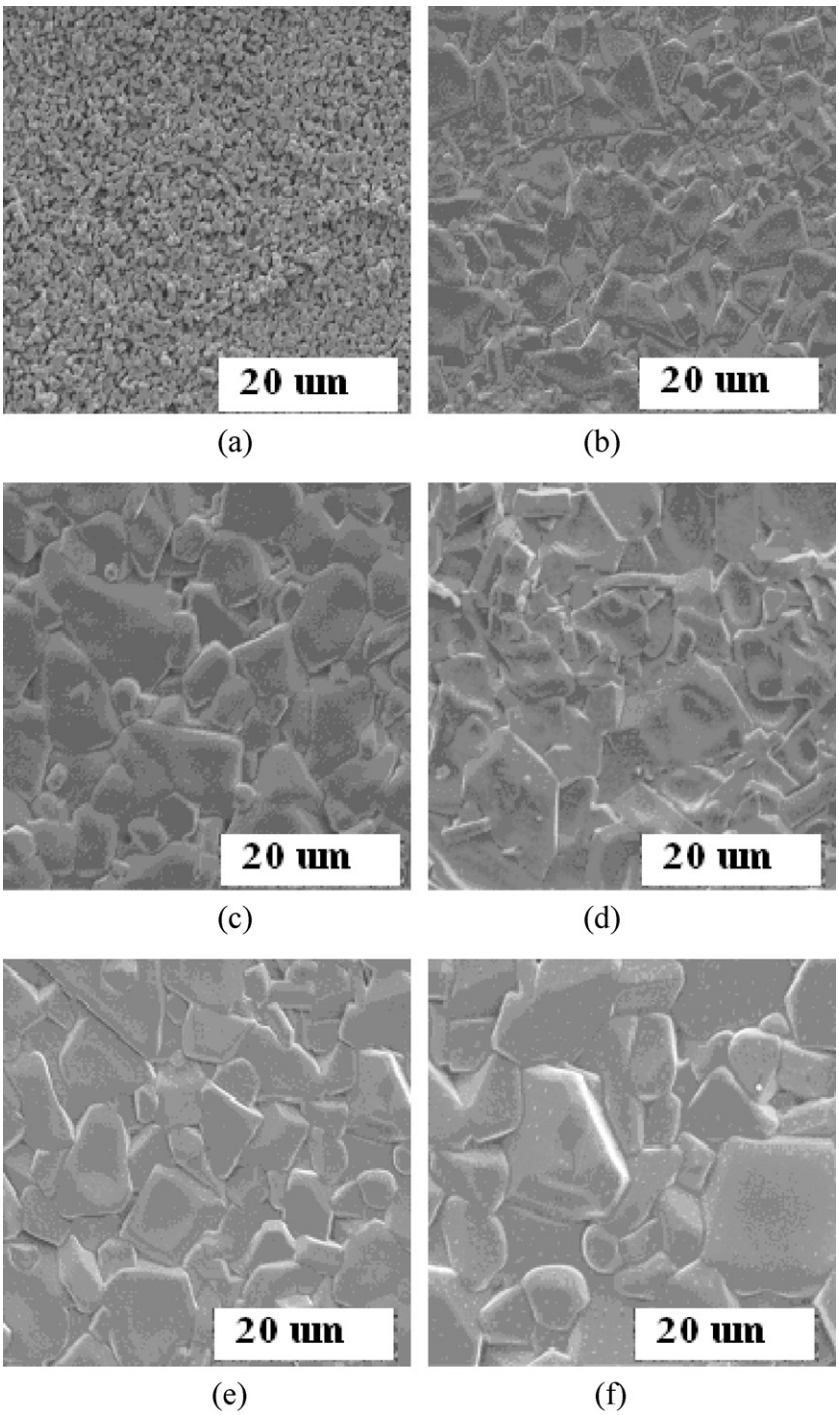
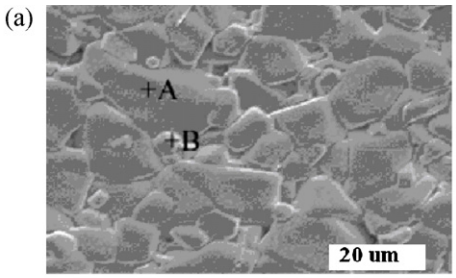


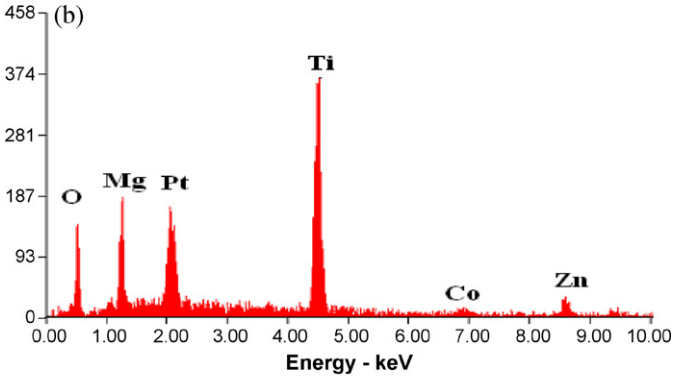
Fig. 3. SEM micrographs of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ doped $BaCu(B_2O_5)$ ceramics sintered at (a) 900 °C, (b) 925 °C, (c) 950 °C, (d) 975 °C, (e) 1000 °C and (f) 1025 °C for 4 h.

increased with sintering temperature. After reaching a maximum at 950 °C, it decreased.

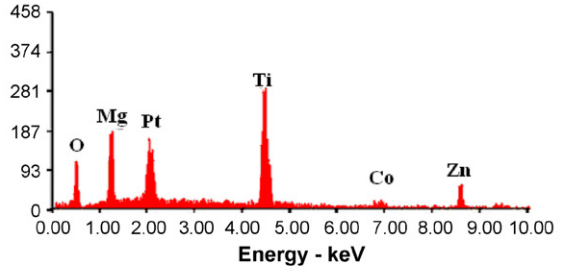
Fig. 6 shows the dielectric constants curves of the $(Mg_{0.7}Zn_{0.3})0.95Co_{0.05}TiO_3$ with 5 wt.% and 7 wt.% BCB doped ceramics at various sintering temperatures for 4 h. The relationship between ε_r values and sintering temperature revealed the same trend as that between density and sintering temperature since higher density means lower porosity. The dielectric constant slightly increased with increasing sintering temperature. ε_r values of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics increased from 17.27 to 18.5 when the sintering temperature was increased from 900 to 950 °C. A maximum ε_r value of 18.5 was obtained $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ with 7 wt.% BCB ceramics sintered at 950 °C for 4 h.

Microwave dielectric loss can be divided into intrinsic loss and extrinsic loss. Intrinsic losses are mainly caused by lattice vibration modes while extrinsic losses are dominated by second phases, oxygen vacancies, grain sizes and densification or porosity. Interfacial polarization is thought to play an important role in porous materials. The quality factor values $(Q \times f)$ of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramic at various sintering temperatures are shown in Fig. 7. With increasing sintering temperature, the $Q \times f$ value increased to a maximum value and then decreased. A maximum $Q \times f$ value of 35,000 GHz was obtained for $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramic at





Spot A(big grain): (atom%) ($(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ phase): Mg K: 14.67, Co K: 2.13, Zn-L: 8.61, Ti K: 16.01, O K: 58.58.



Spot B (small grain)(atom%): Mg K: 14.67, Co K: 2.13, Zn-L: 8.61, Ti K: 16.01, O K: 58.58.

Fig. 4. (a) The marks of SEM for the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics sinter at 950 °C and (b) EDX data of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ doped $BaCu(B_2O_5)$ ceramics for spots A–B.

950 °C. The degradation of the $Q \times f$ value can be attributed to abnormal grain growth at higher sintering temperatures, as shown in Fig. 3. The microwave dielectric loss is mainly caused by the lattice vibrational modes, pores, second phases, impurities, and lattice defects. Relative density also plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials.

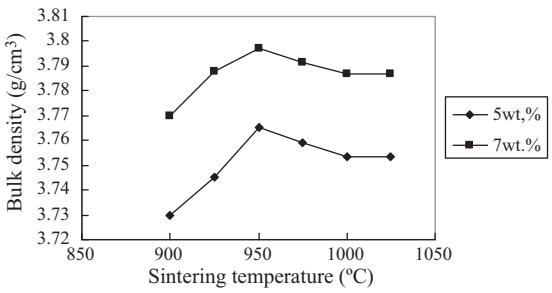


Fig. 5. Bulk density of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ doped $BaCu(B_2O_5)$ ceramics as a function of the sintering temperature.

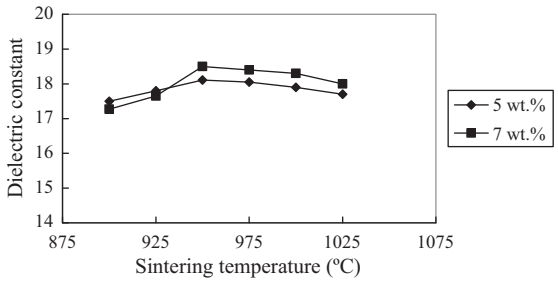


Fig. 6. Dielectric constants curves of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ doped $BaCu(B_2O_5)$ ceramics at different sintering temperatures for 4 h.

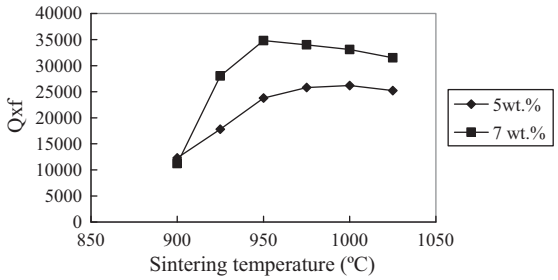


Fig. 7. $Q \times f$ and τ_f values of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ doped $BaCu(B_2O_5)$ ceramics as a function of the sintering temperature.

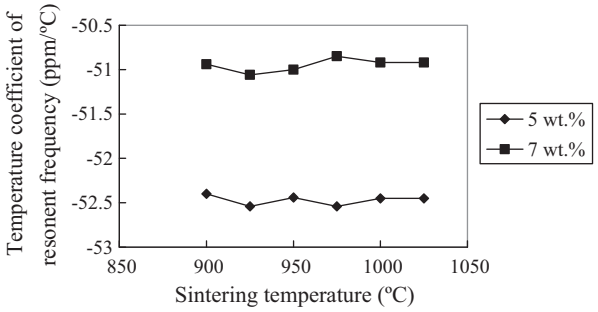


Fig. 8. τ_f values of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ doped $BaCu(B_2O_5)$ system sintering at different temperatures for 4 h.

Fig. 8 illustrates the τ_f values of the $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramic sintered at various sintering temperatures. The temperature coefficient of resonant frequency (τ_f) is known to be governed by the composition, the additives, and the second phase of the material. Because the τ_f values of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}$ and BCB are −65 and −32 ppm/°C, respectively, increasing BCB content makes the τ_f value more positive.

4. Conclusions

The dielectric properties of $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ doped BCB ceramic were investigated. With the partial replacement of $(Mg_{0.7}Zn_{0.3})$ by Co, $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ had excellent dielectric properties with an ε_r ~20, $Q \times f$ ~163,560 GHz, and a τ_f ~−61 ppm/°C after being sintered at a low temperature of 1200 °C. The sintering temperature of ceramics was effectively reduced to 950 °C from 1200 °C with reasonably good $Q \times f$ and ε_r due to added BCB sintering aids. Addition of 7 wt.% BCB in $(Mg_{0.7}Zn_{0.3})_{0.95}Co_{0.05}TiO_3$ ceramics sintered at 950 °C showed excellent dielectric properties of $\varepsilon_r = 18.5$, $Q \times f = 35{,}000$ GHz and $\tau_f = -51$ ppm/°C, which represented a very promising candidates as LTCC dielectric materials for LTCC applications.

Acknowledgements

This work was financially sponsored by the National Science Council of Taiwan under grant NSC-99-2221-E-309-002.

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