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Short communication

Dielectric properties of B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ ceramics at microwave frequency

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Abstract

Microwave dielectric properties and microstructure of $0.98CeO_2$–$0.02CaTiO_3$ ceramics with B_2O_3 additions prepared with the conventional solid-state route have been investigated. $0.98CeO_2$–$0.02CaTiO_3$ ceramics can be sintered at 1290 °C for 4 h due to the sintering aid effect resulting from the B_2O_3 additions. At sintering temperature of 1380 °C for 4 h, $0.98CeO_2$–$0.02CaTiO_3$ ceramics with 0.25 wt% B_2O_3 addition possess a dielectric constant (ε_r) of 21.3, a $Q \times f$ value of 60,000 (at 8 GHz) and a temperature coefficient of resonant frequency (τ_f) of −41 ppm/°C.

Keywords: $0.98CeO_2$–$0.02CaTiO_3$ ceramic; Microwave dielectric properties

1. Introduction

Microwave dielectric materials of a high dielectric constant, a high quality factor and a stable temperature coefficient of resonant frequency have been extensively researched because they can be used as high performance dielectric resonators at microwave frequencies [1,2]. Wireless technologies such as cellular phones and global positioning systems have been making rapid progress due to the improved quality of microwave dielectric resonators. High dielectric constant material can effectively reduce the size of resonators since the wavelength (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_o) in vacuum ($\lambda = \lambda_o/\sqrt{\varepsilon_r}$). The inverse of the dielectric loss ($Q = 1/\tan\delta$) is required to be high for achieving prominent frequency selectivity and stability in microwave transmitter components. In addition, a small temperature coefficient of the resonant frequency is required to ensure stability of the microwave components at different working temperature. Several compounds such as (Zr,Sn)TiO_4, Ba($Mg_{1/3}Ta_{1/3}$)O_3 and (Mg, Ca)TiO_3 have therefore been developed [1–4]. CeO_2 has been widely used as a substrate or buffer layer for superconducting microwave devices since it provides a high quality factor, excellent lattice matching and a good matching for thermal expansion. It also possesses suitable microwave dielectric properties ($\varepsilon_r \sim 23$, $Q \times f \sim 65{,}000$, $\tau_f \sim -53$ ppm/°C) [5,6] for applications in dielectric resonators. To compensate the τ_f value, $CaTiO_3$ ($\varepsilon_r \sim 170$, $Q \times f \sim 3500$, $\tau_f \sim 800$ ppm/°C) [7] with positive τ_f value was introduced to form a solid solution $(1-x)CeO_2$–$xCaTiO_3$. With $x = 0.02$, the maximum density and highest $Q \times f$ value were ~6.87 g/cm^3 and 73,000 GHz, respectively [5]. However, they require high sintering temperatures (1600–1650 °C).

Liquid phase sintering by adding glass or other low melting point material was found to effectively lower the firing temperature of the ceramics [8,9]. The microwave dielectric properties of dielectric resonators were also significantly affected by the liquid sintering temperature due to the development of microstructure at low sintering temperature or the reaction between the host material and addition. In this paper, due to the high density and high $Q \times f$ value for $0.98CeO_2$–$0.02CaTiO_3$ ceramics, B_2O_3 was chosen as a sintering aid to reduce the sintering temperature of $0.98CeO_2$–$0.02CaTiO_3$ ceramics. The crystalline phases, microstructures and the microwave dielectric

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properties of B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ ceramics are reported.

2. Experimental

Samples of $0.98CeO_2$–$0.02CaTiO_3$ were synthesized by conventional solid-state reaction. The starting materials were mixed according to a stoichiometric ratio. A small amount of B_2O_3 (0.25, 1 and 2 wt%) was added as a sintering aid. $CaTiO_3$ powder was fabricated by high purity oxide powders (>99.9%) of $CaCO_3$ and TiO_2 which were mixed for 24 h with distilled water and calcined at 1100 °C for 4 h. The calcined powder $CaTiO_3$ and high purity oxide powders (>99.9%) CeO_2 and B_2O_3 were weighed and mixed for 24 h with distilled water. The mixed powder was ground and sieved through a 100-mesh screen. The mixed powders were then re-milled for 24 h with PVA solution as a binder. Pellets with 11 mm in diameter and 5 mm in thickness were pressed using an uniaxial press. A pressure of 2000 kg/cm^2 was used for all samples. After debinding, these pellets were sintered at temperatures of 1230–1380 °C for 4 h in air.

The powder and bulk X-ray diffraction (XRD, Rigaku D/Max III.V) spectra were collected using Cu Kα radiation (at 30 kV and 20 mA) and a graphite monochromator in the 2θ range 20–60°. Microstructural observations and analysis of sintered surfaces were performed by scanning electron microscopy (SEM, Philips XL-40FEG).

The bulk densities of the sintered pellets were measured by the Archimedes method. The dielectric constant (ε_r) and quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman [10] dielectric resonator method as modified and improved by Courtney [11]. The dielectric resonator was positioned between two brass plates. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. The same technique was applied to measure the temperature coefficient of resonant frequency (τ_f). The test set was placed over a thermostat in the temperature range from +25 to +80 °C.

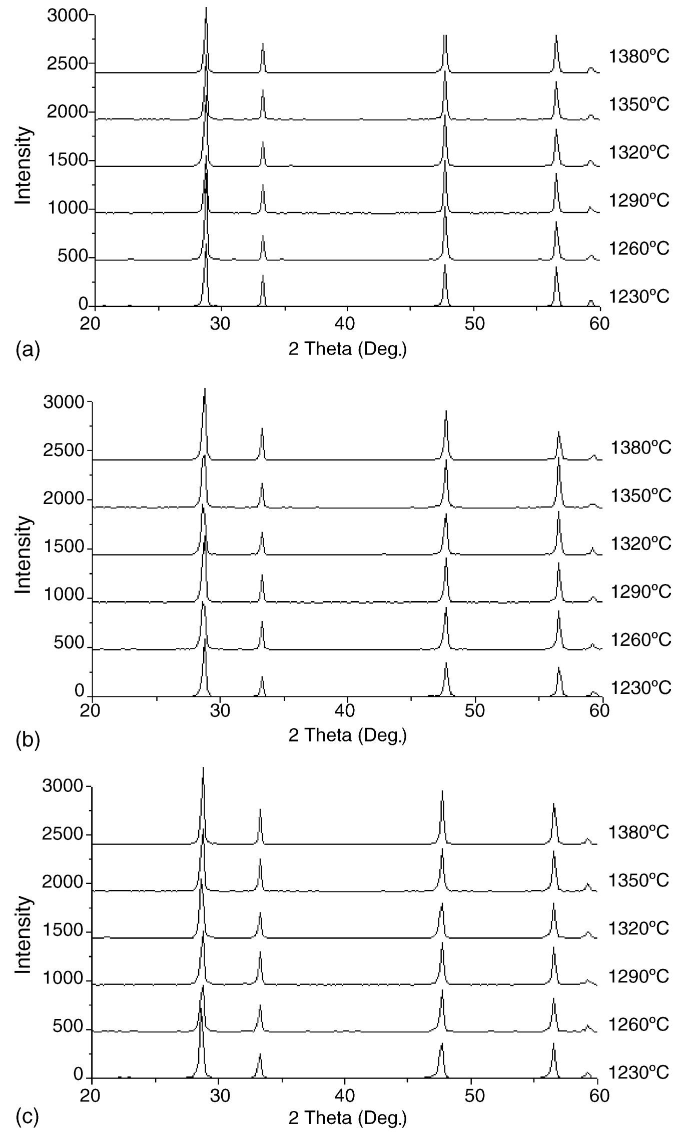

Fig. 1. X-ray diffraction patterns of $0.98CeO_2$–$0.02CaTiO_3$ ceramics at different sintering temperatures (a) 2 wt%B_2O_3 addition, (b) 1 wt% B_2O_3 addition and (c) 0.25 wt% B_2O_3 addition.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of various B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ ceramics at different sintering temperatures (1230–1380 °C). All of the XRD profiles of the ceramics can be indexed by a near cubic fluorite-type structure. The X-ray diffraction patterns of the $0.98CeO_2$–$0.02CaTiO_3$ solid solution have not changed significant with various B_2O_3 additions for sintering temperatures of 1230–1380 °C. Second phase was not observed at the level of various B_2O_3 additions since detection of a minor phase by X-ray diffraction at these levels is extremely difficult.

Microstructural photographs of B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ surfaces for various sintering temperatures (1230–1380 °C) are demonstrated in Fig. 2. The grain size increased with increasing sintering temperature as well as the amount of B_2O_3 addition due to the sintering aid effect. At the level of 1–2 wt% B_2O_3 additions, rapid grain growth was observed for higher sintering temperatures. This may directly affect the microwave dielectric properties of the ceramics.

The density of the B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ ceramics at different sintering temperature is shown in Fig. 3. It indicates that densities of 5.0–6.23 g/cm^3 were obtained for B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ ceramics at sintering temperatures from 1230 to 1380 °C. The density increased with increasing sintering temperature due to enlarged grain growth as observed in Fig. 2, and it was also influenced by B_2O_3 additions. However, the sintering temperature of the maximum value of density for various additions decreased with increasing B_2O_3 additions due to rapid grain growth. With 0.25 wt% B_2O_3 addition, the density increased with increasing sintering temperature, and the maximum density was found to be 6.23 g/cm^3 at 1380 °C. It is suggested that more B_2O_3 addition is not needed to densify the ceramics.

Fig. 4 demonstrates the variation of dielectric constant of $0.98CeO_2$–$0.02CaTiO_3$ ceramics with different amounts of B_2O_3 additions as a function of the sintering temperature. The relationship between ε_r and sintering temperature reveals the same trend as that between density and sintering temperature since higher density means lower porosity. The dielectric constant increases slightly with increasing sintering temperature. The increase of ε_r could be explained by the higher density. With 0.25 wt% B_2O_3 addition, a ε_r value of 21.3 was obtained for $0.98CeO_2$–$0.02CaTiO_3$ ceramics sintered at 1380 °C.

The microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores and any secondary phases. The density also plays an important role in controlling the dielectric loss as has been shown for other microwave dielectric materials. Fig. 5 shows $Q \times f$ values of $0.98CeO_2$–$0.02CaTiO_3$ ceramics with various B_2O_3 additions at different sintering temperatures. The $Q \times f$ values of $0.98CeO_2$–$0.02CaTiO_3$ ceramics increased with increasing sintering temperature. However, a decrease in $Q \times f$ was observed at temperatures higher than 1350 °C with 1 wt% B_2O_3 addition and 1320 °C with 2 wt% B_2O_3 addition. With 0.25 wt% B_2O_3 addition, $Q \times f$ increased from 39,500 to 60,000 GHz as the sintering temperature increased from 1230 to 1380 °C for 4 h. This is consistent with the variation in density. Furthermore, higher B_2O_3 contents may degrade the $Q \times f$ value of $0.98CeO_2$–$0.02CaTiO_3$ ceramics since the grain boundary phases and rapid grain growth were more pronounced at higher sintering temperatures, as observed in Fig. 2. This may explain the decrease in $Q \times f$ values for $0.98CeO_2$–$0.02CaTiO_3$ ceramics with higher B_2O_3 additions at 1380 °C.

The temperature coefficients of resonant frequency (τ_f) of B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ ceramics at different

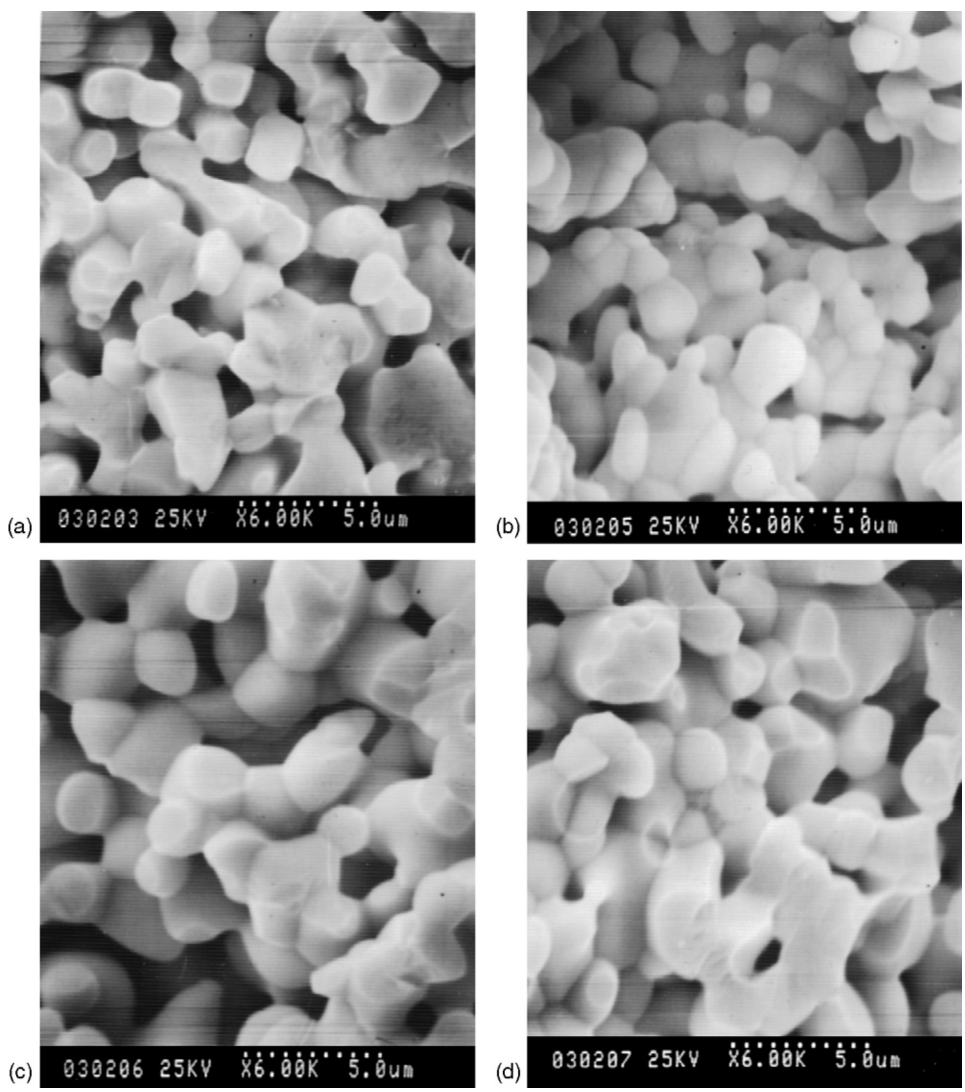

Fig. 2. SEM photographs of $0.98CeO_2$–$0.02CaTiO_3$ ceramics with different B_2O_3 additions at different sintering temperatures: (a) 0.25 wt% B_2O_3 1260 °C; (b) 0.25 wt% B_2O_3 1290 °C; (c) 0.25 wt% B_2O_3 1320 °C; (d) 0.25 wt% B_2O_3 1350 °C; (e) 0.25 wt% B_2O_3 1380 °C; (f) 1 wt% B_2O_3 1380 °C; (g) 2 wt% B_2O_3 1380 °C.

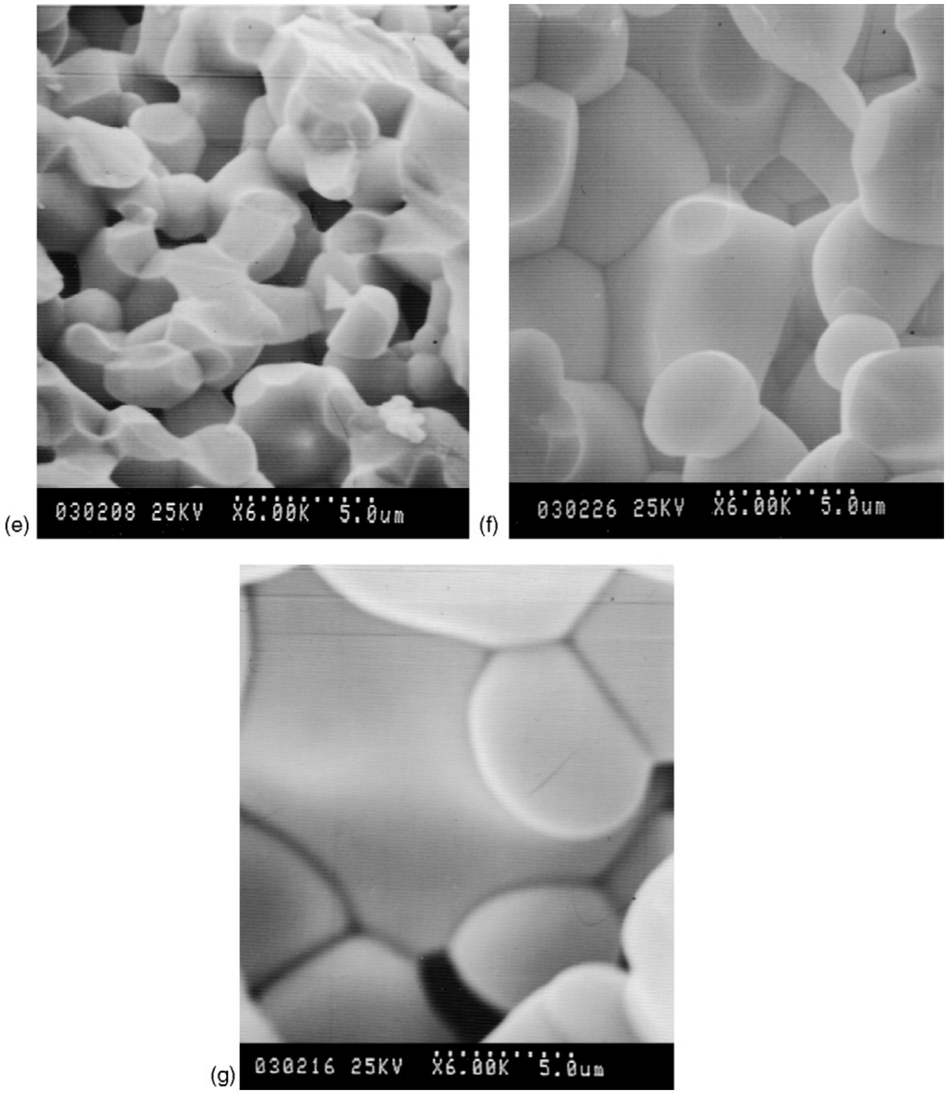

Fig. 2. (*Continued*).

sintering temperatures are illustrated in Fig. 6. The temperature coefficient of resonant frequency is well known to be related to the composition, the additives and the presence of secondary phases. It seems that higher B_2O_3 contents shift τ_f to more positive values. It varied from −42 to −29 ppm/°C as the amount of B_2O_3 addition increased from 0.25 to 2 wt%. There was no significant change in τ_f for a fixed B_2O_3 addition at different sintering temperatures.

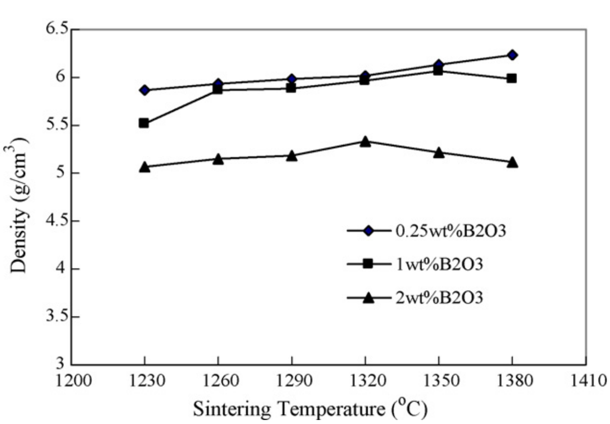

Fig. 3. Dependence of sintering temperature of $0.98CeO_2$–$0.02CaTiO_3$ ceramics on relative density with various B_2O_3 additions.

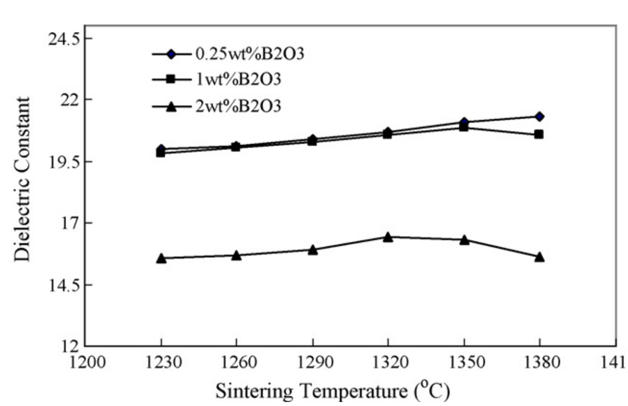

Fig. 4. Dependence of sintering temperature of $0.98CeO_2$–$0.02CaTiO_3$ ceramics on dielectric constant with various B_2O_3 additions.

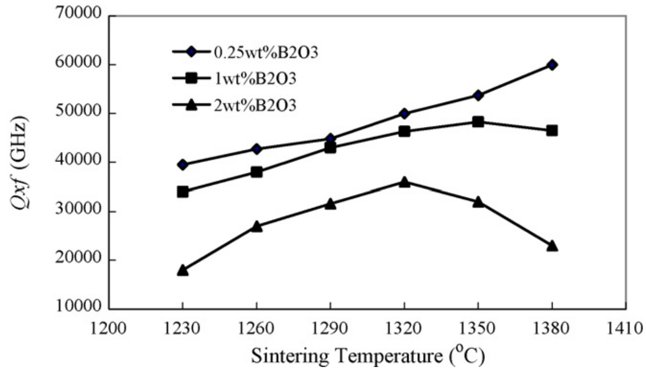

Fig. 5. Dependence of sintering temperature of $0.98CeO_2$–$0.02CaTiO_3$ ceramics on quality factor ($Q \times f$) with various B_2O_3 additions.

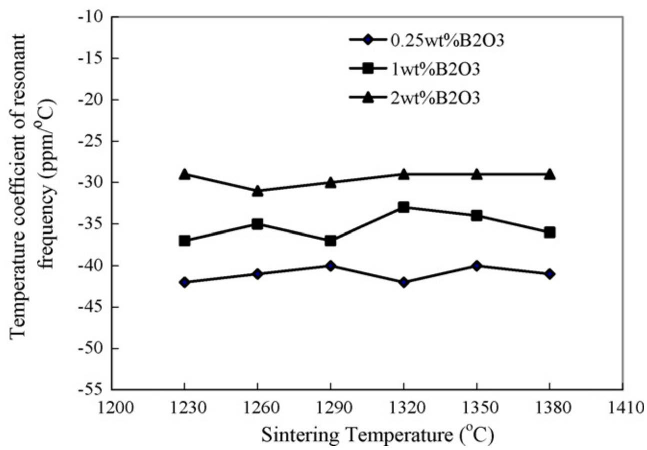

Fig. 6. Dependence of sintering temperature of $0.98CeO_2$–$0.02CaTiO_3$ ceramics on τ_f value with various B_2O_3 additions.

4. Conclusion

The dielectric properties of B_2O_3-doped $0.98CeO_2$–$0.02CaTiO_3$ ceramics were investigated. A distinct sintering temperature reduction (100–200 °C) can be achieved by adding B_2O_3 to $0.98CeO_2$–$0.02CaTiO_3$ ceramics. With 0.25 wt% B_2O_3 addition, a dielectric constant of 21.3, a $Q \times f$ value of 60,000 GHz and a τ_f value of -41 ppm/°C were obtained for $0.98CeO_2$–$0.02CaTiO_3$ ceramics at 1380 °C for 4 h. The decrease in $Q \times f$ value at higher additions and sintering temperatures was attributed to rapid grain growth. B_2O_3 additive effectively lowers the sintering temperature and can promote the $Q \times f$ value of the $0.98CeO_2$–$0.02CaTiO_3$ ceramics.

Acknowledgement

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