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Sintering and dielectric properties of Al_2O_3 ceramics doped by TiO_2 and CuO

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Abstract The effects of CuO and TiO_2 additives on the microstructure and microwave dielectric properties of Al_2O_3 ceramics were investigated. Al_2O_3 ceramics with CuO and TiO_2 additions can be well sintered to achieve 93~98% theoretical densities below 1,360 °C due to Ti_4Cu_2O liquid phase sintering effect. The *Qf* values decreased with increasing CuO and TiO_2 content, due to the formation of the second phase Ti_4Cu_2O. However, the varying behaviors of the dielectric constant (ε_r) and temperature coefficients (τ_f) were associated with phase constitutions, as a result of the change of CuO and TiO_2content. The τ_f can be shifted close to 0 ppm/°C by controlling the content of CuO and TiO_2. The specimens with 0.5 wt.% CuO and 7 wt.% TiO_2 sintered at 1,360 °C for 4 h showed ε_r of 11.8, *Qf* value of 30,000 GHz, and τ_f of −7 ppm/°C.

Keywords Liquid-phase sintering · Dielectric properties · Alumina · Microwave ceramics

1 Introduction

In recent years, mobile communication system has prevailed in a worldwide range and the techniques of internet have been developed fast. These developments have caused the information capacity of mobile communication increasing exponentially. The competitions for communication wave band have been more and more furious. Mobile communication should be developed to a higher frequency in order to utilize frequency resource sufficiently and widen the wave width. The wave band of 5.8 GHz has been opened. For that the microwave components based on microwave dielectric ceramics have to fulfill higher requirements. Therefore, microwave dielectric ceramics used in high frequency has become a research focus.

Several compounds such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$, $(Mg,Ca)TiO_3$ have been developed for the microwave applications [1–4]. Al_2O_3 ceramics exhibits good microwave dielectric properties of low dielectric constant (ε_r~10) and good quality factor (*Qf*~50,000 GHz). However, Al_2O_3 ceramics requires a very high sintering temperature (1600 °C) and have a very large temperature coefficients of resonant frequency (τ_f=−60 ppm/°C) [5]. For practical applications, it is necessary to reduce the sintering temperature and temperature coefficients of resonant frequency of Al_2O_3 ceramics.

In order to shift the τ_f value of Al_2O_3 ceramics, TiO_2 with positive τ_f value (τ_f=+450 ppm/°C) [6] was introduced to form Al_2O_3–TiO_2 ceramics. Tzou et al. reported that Al_2O_3–TiO_2 ceramics containing MgO–CaO–SiO_2–Al_2O_3 glass addition could be sintered at 1,250~1,350 °C and achieved τ_f ~0 ppm/°C by adjusting the sintering temperature and TiO_2 content. However, the *Qf* value of Al_2O_3 ceramics decreased to 9,578 GHz because of the formation of Al_2TiO_5 phase and glass phase [7]. Ohishi et al found that the Al_2TiO_5 phase disappeared by annealing treatment and a near-zero τ_f with excellent microwave dielectric properties was obtained in 0.9 Al_2O_3–0.1 TiO_2 ceramics sintered 1,350 °C for 2 h [8].

In this study, CuO and TiO_2 multiple additives were added into Al_2O_3 ceramics to lower the sintering temperature and to improve the *Qf* and τ_f values. The influences of CuO and TiO_2 additions on the microstructures and the microwave dielectric properties of Al_2O_3 ceramics were discussed.

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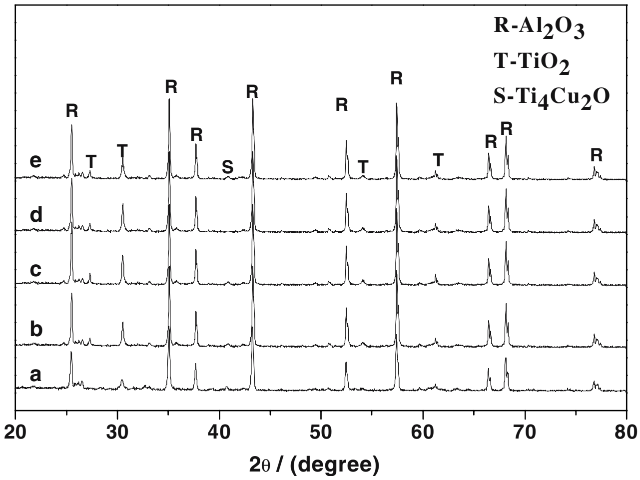

Fig. 1 X-ray diffraction patterns of Al_2O_3 ceramics with **a** 1.0 wt.% CuO-3.0 wt.% TiO_2, **b** 1.0 wt.% CuO-7.0 wt.% TiO_2, **c** 1.0 wt.% CuO-10 wt.% TiO_2, **d** 0.5 wt.% CuO-7 wt.% TiO_2, and **e** 1.5 wt.% CuO-7 wt.% TiO_2 sintered at 1,320 °C for 4 h

2 Experimental procedures

Samples of Al_2O_3+xCuO$+y$$TiO_2$ ($x = 0.5 \sim 1.5$wt.%, $y = 3 \sim 10$wt.%) were synthesized by conventional solid-state reaction methods using high-purity α–Al_2O_3, CuO and TiO_2(≥99%). The starting materials were mixed according to the desired stoichiometry, and then ground in distilled water for 24 h in a balling mill with zircon balls. The mixtures were dried, forced through a 300 mesh sieve, and pressed into pellets 11 mm in diameter and 5 mm thickness by uniaxial pressing at 1,000 kg/cm^2. The pellets were sintered at temperatures of 1,240~1,400 °C for 4 h in air atmosphere.

The crystalline phases of the sintered ceramics were identified from X-ray diffraction patterns. The microstructure of sintered compacts was taken from polished and fractured surfaces by scanning electron microscopy (SEM). For differential thermal analysis (DTA) experiments, the samples were fired at a heating rate of 5 °C/min in flowing air. The bulk densities of the pellets were measured by the Archimedes method. Microwave dielectric constants ε_r and the quality values *Qf* at microwave frequencies (9~9.5 GHz) were measured by Hakki-Coleman dielectric resonator method [9] using an Agilent 8719ET(50 MHz~13.5 GHz) network analyzer. Temperature coefficient of resonant frequency (τ_f) (ppm/°C) was also measured by the same method with changing temperature mainly from 25 to 80 °C and calculated from the equation:

$$\tau_f = (f_{80} - f_{25})/(f_{25} \times 55) \times 10^6$$

where f_{80} and f_{25} represent the resonant frequency at 80 and 25 °C, respectively.

In our experiment, the test data of the apparent densities, dielectric properties shown in Figures is the average value of three samples. The error of the apparent densities, dielectric constants ε_r, the quality values *Qf*, and temperature coefficient of resonant frequency τ_f among three samples is about 2, 1, 5, and 5%, respectively.

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of Al_2O_3 ceramics doped with CuO and TiO_2 sintered at 1,320 °C for 4 h. The XRD diffraction patterns showed the α–Al_2O_3 phases existed as the main crystalline phases associated with TiO_2 as minor phases. A small amount of the second phase Ti_4Cu_2O was detected. The intensity of TiO_2 phase peaks is enhanced with the increase of TiO_2 content. The intensity of TiO_2 phase peaks is weakened and the intensity of Ti_4Cu_2O phase peaks is enhanced with the increase of CuO content. In the study of the Al_2O_3–TiO_2 ceramics doped with MgO–CaO–SiO_2–Al_2O_3 glass, Tzou et al found that Al_2TiO_5 phase which caused a bigger decrease in *Qf* was formed as the second phase [7]. However, in our studies, it is interesting to note that the Al_2TiO_5 phase is not observed for all of the prepared samples. It indicates that CuO addition prevent the formation of Al_2TiO_5 phase.

The average apparent densities of Al_2O_3 ceramics doped with CuO and TiO_2 as a function of sintering temperatures are illustrated in Fig. 2. The sintering temperature of the pure Al_2O_3 ceramics is higher than 1600 °C. In contrast to that, the Al_2O_3 samples with CuO–TiO_2 have attained 93~98% theoretical density (The theoretical densities of Al_2O_3, TiO_2, and Ti_4Cu_2O are 3.99, 4.25 and 3.78 g/cm^3, respectively, estimated from the XRD patterns) below 1360 °C. For the specimen with 0.5 wt% CuO-7 wt.% TiO_2, 1 wt.% CuO-3 wt.% TiO_2, and 1 wt.% CuO-10 wt.% TiO_2, Al_2O_3 ceramics densities increased drastically with

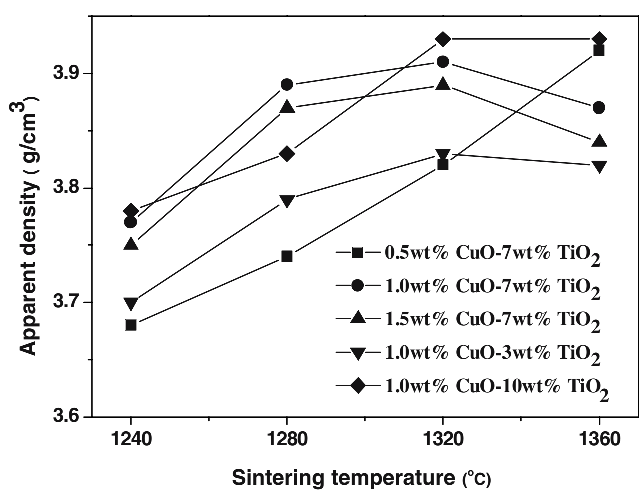

Fig. 2 The average apparent densities of Al_2O_3 ceramics doped with CuO and TiO_2 vs. sintering temperature

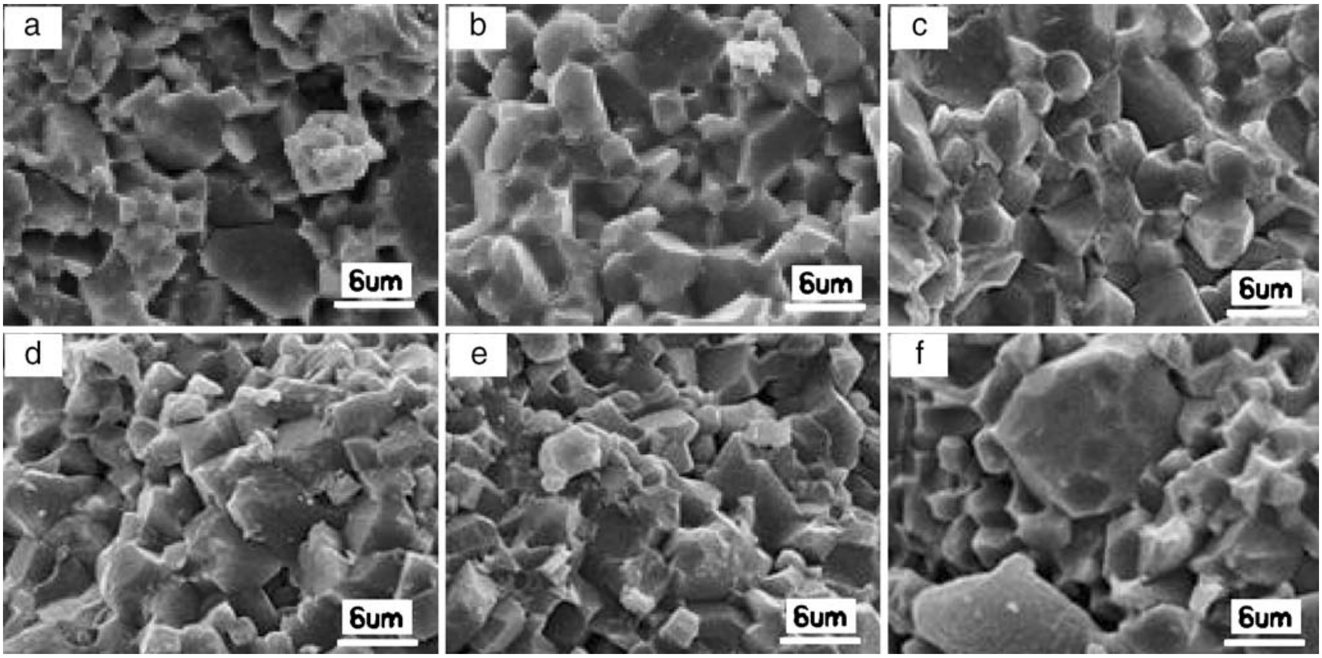

Fig. 3 The SEM micrograph of Al_2O_3 Ceramics with **a** 0.5 wt.% CuO-7 wt.% TiO_2, **b** 1.0 wt.% CuO-7 wt.% TiO_2, **c** 1.5 wt.% CuO-7 wt.% TiO_2, **d** 1.0 wt.% CuO-10 wt.% TiO_2 sintered at 1,320 °C, and with **e** 0.5 wt.% CuO-7 wt.% TiO_2, **f** 1.0 wt.% CuO-7 wt.% TiO_2 sintered at 1,360 °C

increasing sintering temperature and then saturated. However, for the specimen with 1 wt.% CuO-7 wt.% TiO_2, and 1.5 wt.% CuO-7 wt.% TiO_2, the densities initially increased with increasing sintering temperature and then decreased. The density decrease of samples sintered at 1,360 °C might be caused by overfiring. And the overfiring could result in abnormal grain growth, as clearly shown in Fig. 3f, which hinders the densification of Al_2O_3 ceramics. The maximum density at a certain temperature increased with increasing TiO_2 content and with decreasing CuO content due to the increase of TiO_2 (confirmed by phase analyses in Fig. 1.) which showed higher than Al_2O_3 and Ti_4Cu_2O.

The SEM photographs of Al_2O_3 ceramics with different amount of additives are illustrated in Fig. 3. Most of the samples have equiaxed crystal grains. At 1,320 °C, the section of Al_2O_3 ceramics with 0.5 wt.% CuO and 7 wt.% TiO_2 were porous. However the uniform grain growth and a reduction in porosity were observed for Al_2O_3 ceramics with 1.0 wt.%, 1.5 wt.% CuO and 7 wt.% TiO_2. The effect of CuO and TiO_2 was demonstrated not only the decrease of the sintering temperature, but also the improved grain growth of ceramics. When sintering temperature increased to 1,360 °C, the sample with 1.0 wt.% CuO and 7 wt.% TiO_2 gave exaggerated grain growth with inhomogeneous microstructure. The minimum grain size was 2 um and the maximum was 15 um, and the proportion of the large grain increased. The sample with 0.5 wt.% CuO and 7 wt.% TiO_2 was dense, and the grain size increased.

Figure 4. shows the differential thermal analysis (DTA) curves of pure Al_2O_3 and Al_2O_3 doped with 0.5 wt.% CuO-7 wt.% TiO_2. The endothermic or euthermic peak is not observed for the pure Al_2O_3 sample. However, the DTA cure of Al_2O_3 doped with 0.5 wt.% CuO-7 wt.% TiO_2 shows an endothermic peak at 1,121.6 °C, which is the melting temperature of the phase Ti_4Cu_2O as shown in Fig. 1. Thus, when the Al_2O_3 ceramics doped with CuO and TiO_2 were sintered, the low melting phase Ti_4Cu_2O

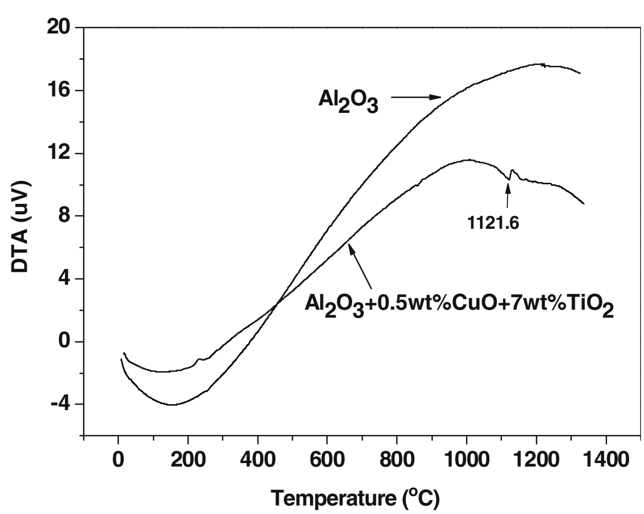

Fig. 4 DTA curves of pure Al_2O_3 and Al_2O_3 doped with 0.5 wt.% CuO-7 wt.% TiO_2

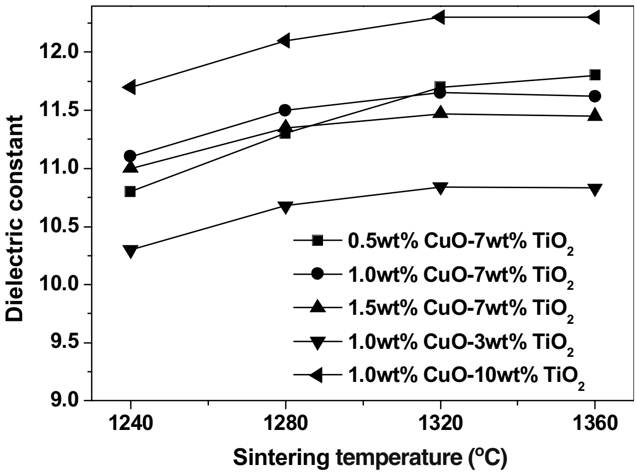

Fig. 5 The average dielectric constants of Al_2O_3 ceramics with CuO and TiO_2 vs. sintering temperature

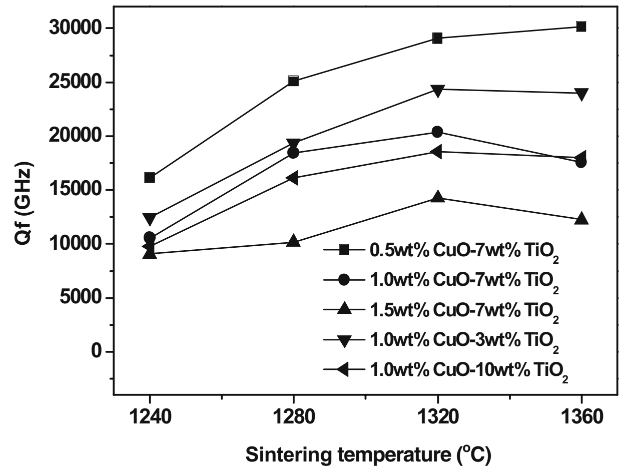

Fig. 6 The average *Qf* values of Al_2O_3 ceramics with CuO and TiO_2 vs. sintering temperature

formed due to the reaction between with CuO phase and TiO_2 phase at a certain temperature (confirmed by the analyses in Fig. 1. and reference [10]). The decrease of Al_2O_3 ceramic sintering temperature was caused by the liquid-phase effect of Ti_4Cu_2O which was melted about 1,126 °C.

The average dielectric constant of Al_2O_3 ceramics with CuO and TiO_2 as functions of their sintering temperatures is shown in Fig. 5. The relationship between ε_r values and sintering temperatures reveals basically the same trend with those between bulk densities and sintering temperatures, because higher density means lower porosity (ε_r=1). The ε_r values of Al_2O_3 ceramics with constant amount of TiO_2 decreased with increasing CuO content, which might be attributed to the gradual increase of Ti_4Cu_2O and reduction of TiO_2 with higher ε_r value (~100) [6] illustrated in Fig. 1. For the specimens with the same CuO content, the ε_r values increased with increasing TiO_2 content. However, the average dielectric constant varying with the CuO and TiO_2 content was not consistent with the variation of density illustrated in Fig. 2. It was observed that Al_2O_3 ceramics with 0.5 wt.% CuO and 7 wt.% TiO_2 sintered at 1,280 °C showed lower density than ones with 1.0 wt.% CuO and 3 wt.% TiO_2, but higher ε_r values than ones with 1.0 wt.% CuO and 3 wt.% TiO_2. The dielectric constant is dependent on the density and phase constituents. In general, higher density results in a higher dielectric constant owing to lower porosity (ε_r=1). It indicates that TiO_2 with higher ε_r value play a chief role in the ε_r variety of Al_2O_3 ceramics.

Figure 6 illustrates the average *Qf* values of Al_2O_3 ceramics with CuO and TiO_2 as a function of their sintering temperatures. For the specimen with 0.5 wt.% CuO-7 wt.% TiO_2, 1 wt.% CuO-3 wt.% TiO_2, and 1 wt.% CuO-10 wt.% TiO_2, The *Qf* values of Al_2O_3 ceramics increased drastically with increasing sintering temperature and then reached a saturation value. However, for the specimen with 1 wt.% CuO-7 wt.% TiO_2, and 1.5 wt.% CuO-7 wt.% TiO_2, the *Qf* values initially increased with increasing sintering temperature and then decreased. It was observed that the *Qf* values decreased with increasing CuO and TiO_2 content. The microwave dielectric loss was mainly caused not only by

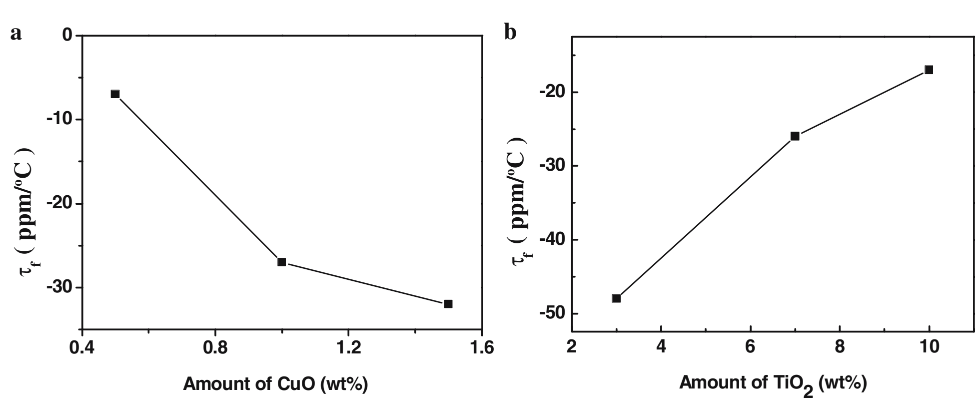

Fig. 7 The average temperature coefficients of resonant frequency (τ_f) of Al_2O_3 ceramics of **a** with 7 wt.% TiO_2, and **b** with 1 wt% CuO sintered at 1,360 °C

the lattice vibration modes, but also by the pores and the second phase [11]. It was reported by Kim et al [12] that a second phase was a more important factor than porosity to reduce the *Qf* values of microwave dielectric ceramics having over 90% of relative density. Thus the increase of CuO and TiO_2 decreased the maximum *Qf* values of Al_2O_3 ceramics due to the increase of the second phase Ti_4Cu_2O with a very low *Qf* value, and the decrease in *Qf* values with the increasing temperature might be attributed to abnormal grain growth, as clearly shown in Fig. 3f [13].

Figure 7 shows the average temperature coefficient of resonant frequency (τ_f) of Al_2O_3 ceramics with CuO and TiO_2 sintered at 1,360 °C. These results suggest that the τ_f values change to negative values with the increase of CuO content and to positive values with the increase of TiO_2 content. The τ_f values of Al_2O_3 and TiO_2 are −60 and 450 ppm/°C, respectively [5, 6]. According to the XRD patterns, as shown in Fig. 1, the intensity of TiO_2 phase is enhanced with the increase of TiO_2 additive, the intensity of TiO_2 phase is weakened and the intensity of Ti_4Cu_2O is enhanced with the increase of CuO additive. The apparent change of τ_f values mentioned above when the content of CuO and TiO_2 changed could be thought as the effect of the crystalline phase. From these results, we can determine that the modification of τ_f was associated with CuO and TiO_2 content. The Al_2O_3 ceramics with 0.5 wt.% CuO and 7 wt.% TiO_2 sintered at 1,360 °C had τ_f of −7 ppm/°C.

4 Conclusion

The microwave dielectric properties and the microstructure of Al_2O_3 ceramics with CuO and TiO_2 additive were investigated. Al_2O_3 ceramics with CuO and TiO_2 can be well sintered to achieve 93~98% theoretical density below 1360°C due to Ti_4Cu_2O liquid phase sintering effect. The microwave dielectric properties of Al_2O_3 ceramics are found to correlate with sintering temperature and the amount of sintering aid. The *Qf* values decreased with increasing CuO and TiO_2 content, due to the formation of second phase Ti_4Cu_2O. However, the behaviors of ε_r and τ_f were associated with phase constitutions, as a result of the change of CuO and TiO_2 content. In this study, the τ_f can be shifted close to 0 ppm/°C by controlling the CuO and TiO_2 content. As sintered at 1,360 °C, Al_2O_3 ceramics with 0.5 wt.% CuO and 7 wt.% TiO_2 additives exhibited good microwave dielectric properties: ε_r=11.8, *Qf*=30,000 GHz, τ_f=−7 ppm/°C.

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