Influence of CuO or MnCO₃ Additive on the Dielectric Properties of Ca₀.₆₅Ti₀.₆₅La₀.₃₅Al₀.₃₅O₃ Ceramics

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Abstract. The influence of CuO or MnCO₃ additive on the sinterability, microstructure and microwave dielectric properties of Ca₀.₆₅Ti₀.₆₅La₀.₃₅Al₀.₃₅O₃, i.e., CTLA, ceramics was investigated in this paper. The results indicated that the density and dielectric properties of CTLA ceramics can be improved by both low-level doping of CuO (up to 1 wt%) and MnCO₃ (up to 0.75 wt%). The sintering temperature of CTLA ceramics with addition of CuO/MnCO₃ can be effectively reduced from 1450°C to 1320°C due to the liquid phase effect. No secondary phase was observed for the addition at the amount of 0.5-1 wt% CuO and 0.25-0.75 wt% MnCO₃. With the addition of CuO/MnCO₃, the dielectric constant (εᵣ) and the temperature coefficient of resonant frequency (τᵣ) of the samples were not significantly affected, while the unloaded quality factors Q were effectively promoted. Excellent microwave dielectric properties were achieved for the ceramic Ca₀.₆₅Ti₀.₆₅La₀.₃₅Al₀.₃₅O₃ + 0.75wt% CuO/ MnCO₃ sintered at 1320°C for 2 h, with values of Q×f = 32,800 GHz, εᵣ = 43 and τᵣ = +10 ppm/°C.

1. Introduction

With the advance of wireless technologies, it is of key importance to develop microwave dielectric ceramics (MWDC). The requirements for microwave ceramics are a high dielectric constant (εᵣ), a low dielectric loss (high Q value) and a temperature-stable resonant frequency (τᵣ≈0 ppm/°C). By increasing εᵣ, we can reduce the size of the ceramic component and therefore reduce the overall size of the telecommunications device, and the signal quality of filter is improved by increasing the Q value of the resonators [1].

CaTiO₃ is an orthorhombic distorted perovskite [2] at room temperature with εᵣ=170, Q×f =3,500 GHz and τᵣ≈+800 ppm/°C [3]. In contrast LaAlO₃ is a rhombohedral perovskite at room temperature with εᵣ=23.4, Q×f =68,000GHz and τᵣ=-44ppm/°C [4]. Ceramic material based on the solid solution of CaTiO₃-LaAlO₃ is a promising candidate for microwave frequencies because of its high dielectric constant (τᵣ=44) with high quality factor (Q×f≈32,000GHz) and small or zero τᵣ.

Moon J H et al. [5] first studied the dielectric and sintering properties of (1-x)CaTiO₃-xLaAlO₃ ceramics. A high sintering temperature of 1600°C was required to obtain dense ceramics. Additions of Bi₂O₃-Al₂O₃ or Bi₂O₃-NiO lowered the sintering temperature to 1450°C. However, the additives reduced the Q×f value by at least 15%. The microwave dielectric properties of Q×f 32,500 GHz, εᵣ≈
41 and $\tau_f \approx +5 \text{ ppm/°C}$ were reported for the undoped 0.65CaTiO$_3$-0.35LaAlO$_3$. Jancar B et al. [6] studied the dielectric and sintering properties of (1-x)CaTiO$_3$$-x$ReMO$_3$ (Re=La, Nd, Sm; M=Al, Ga) ceramics. They reported dielectric properties of $Q\times\varepsilon = 30,000$ GHz, $\varepsilon_r = 44$ and $\tau_f = -2 \text{ ppm/°C}$ for 0.65CaTiO$_3$-0.35LaAlO$_3$. However, the high calcinations temperature in the range of from 1350 to 1450°C for 40h and high sintering temperature of 1450°C for 10h were reported.

In this paper, the effects of CuO and MnCO$_3$ additive on the sinterability, microstructure and microwave dielectric properties of Ca$_{0.65}$Ti$_{0.65}$La$_{0.35}$Al$_{0.35}$O$_3$ ceramics are investigated.

2. Experimental procedure

Samples were prepared by conventional solid-state ceramic route using high purity (>99%) of CaCO$_3$, TiO$_2$, La$_2$O$_3$ and Al$_2$O$_3$ as the raw materials. They were weighed according to composition of Ca$_{0.65}$Ti$_{0.65}$La$_{0.35}$Al$_{0.35}$O$_3$ and ball-milled with deionized water in a planetary mill for 2h with zirconia balls. The mixed powders were dried and calcined at 1200°C for 2h in air. The resultant powders added with 0.5-1 wt% CuO (>99%) and 0.25-0.75 wt% MnCO$_3$ (>99%), and then ball milled again in deionized water with zirconia balls for 2h. After drying, the powders were blended with 5% PVA solution, and then granulated, screened through a sieve with 40-mesh, and pressed uni-axially at 200MPa into disks with 13mm in diameter and 2-7mm in thickness with a steel die. The green pellets were then sintered at 1280°C to 1340°C for 2h in air at a rate of 5°C/min, and furnace-cooled to ambient temperature.

Bulk densities of the ceramics were determined by the Archimedes method. Crystalline structures were identified by powder X-ray diffraction (Panalytical X’pert) in the 2θ range from 10° to 90°. The ceramics were observed with scanning electron microscopy (SEM) (Philips XL30). Microwave dielectric properties were measured using an Agilent E8362B vector network analyzer in the range of 1-20GHz. Dielectric constant ($\varepsilon_r$) was measured by the Hakki-Coleman dielectric resonator method [7]. The value of $\tau_f$ was obtained in the range from 25°C to 80°C, and was calculated with following expression.

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}$$

Where $f_1$ and $f_2$ were the resonant frequencies at temperatures of $T_1$ and $T_2$, respectively.

3. Results and discussion

3.1. Phase identification

3.1.1 Effect of the amount of CuO on CTLA ceramics. X-ray diffraction patterns of CuO-doped CTLA ceramics sintered at 1320°C for 2h are shown in Figure 1. It is observed that CTLA belongs to the tetragonal-type crystal structure. No obvious peak of secondary phase is found for the samples with additive CuO in weight percent of 0.5-1.0 due to the fact that detection of a minor phase by XRD is extremely difficult. Since the ionic radius of Ti$^{4+}$ (0.068nm) and Al$^{3+}$ (0.072nm) is similar to that of Cu$^{2+}$ (0.073nm) [8], they might be substituted by Cu$^{2+}$ ion in the ceramics. The total charge of two ions of Cu$^{2+}$ is moreover equal to that of one ion of Ti$^{4+}$, and no charge distortion is induced. Hence, the additive CuO might be substituted into the main structure of CTLA ceramics.

3.2. Effect of the amount of MnCO$_3$ on CTLA ceramics. X-ray diffraction spectra for CTLA ceramics prepared with different levels of MnCO$_3$ sintered at 1320°C for 2h is displayed in Figure 2. The single phase with tetragonal structure is observed for CTLA ceramics doped with 0.25-0.75wt% MnCO$_3$. The results suggest that Mn$^{2+}$ may incorporate into the lattices of Ca$_{0.61}$Ti$_{0.61}$La$_{0.39}$Al$_{0.39}$O$_3$ structure, since the ion radius of Mn$^{2+}$ (0.080 nm) is similar to that of Ti$^{4+}$ (0.068 nm) and Al$^{3+}$ (0.072 nm) [8].
Therefore, MnCO₃ can be used as a useful additive to lower the sintering temperature of CTLA ceramics without changing the crystalline structure of major phase.

![XRD patterns of CTLA with CuO additives sintered at 1320°C for 2h](image1)

**Figure 1.** The XRD patterns of CTLA with CuO additives sintered at 1320°C for 2h (a)0.0wt% (b)0.50wt% (c)0.75wt% (d)1.00wt%

3.2. Densification

3.2.1. *Effect of the amount of CuO on CTLA ceramics.* Bulk density of CTLA ceramics with CuO as a function of sintered temperature is illustrated in Figure 3. The results demonstrate that the relative density of the samples steadily increases with increasing sintering temperature. The density is increased with 0.5wt% CuO addition, then decreased with more CuO addition above 1300°C. The densification might caused by the liquid phase effect of CuO. At higher temperature, the density decreased might due to the low density of liquid phase and the vaporization of CuO. Maximum relative density is found to be 93.93% with 0.5wt% CuO addition at 1320°C.

3.2.2. *Effect of the amount of MnCO₃ on CTLA ceramics.* Bulk density of CTLA ceramics with MnCO₃ as a function of sintered temperature is given in Figure 4. It can be observed that the relative density of the samples steadily increases with increasing sintering temperature. The density is increased with 0.25-0.5wt% MnCO₃ additive, then decreased with more addition of MnCO₃ above 1300°C. Maximum relative density is found to be 93.98% with the addition of 0.25wt% MnCO₃ at 1320°C.

![XRD patterns of CTLA with MnCO₃ additions sintered at 1320°C for 2h](image2)

**Figure 2.** The XRD patterns of CTLA with MnCO₃ additions sintered at 1320°C for 2h (a)0.0wt% (b)0.25wt% (c)0.50wt% (d)0.75wt%

**Figure 3.** Bulk densities of CTLA ceramics with CuO as a function of sintered temperature

**Figure 4.** Bulk densities of CTLA ceramics with MnCO₃ as a function of sintered temperature
3.3. Microstructure

3.3.1. Effect of the amount of CuO on CTLA ceramics. Observation of microstructure for as-sintered CTLA ceramics reveals difference in the samples with different levels of CuO, as displayed in Figure 5(a)-(f). It can be seen that the grain size is about 1-2\( \mu \)m and there are few pores in the samples. For undoped and CuO-doped specimens sintered at 1320°C, there are lots of quadrate grains and the ratio of length to width is about 1:1. Moreover, for additions of 0.50 wt% and 1.00wt% CuO the liquid phase effect is observed in the microstructure, but not for that with 0.75wt% CuO additive. The liquid phase effect may be caused by eutectic of CuO-Cu\(_2\)O-TiO\(_2\) (Cu\(_3\)TiO\(_4\)) [9] at 1070°C. Especially in the case of 1.00wt% CuO additive, the vaporization of CuO is presented as evidence for the liquid phase.

3.3.2. Effect of the amount of MnCO\(_3\) on CTLA ceramics. SEM micrographs of MnCO\(_3\)-doped CTLA ceramics sintered at 1320°C are present in Figure 5(g)-(i). It can be seen that the grain size is about 1-2\( \mu \)m and there are few pores in the samples. Moreover, a little of glass phase is found in the triple region of grains of MnCO\(_3\)-doped specimens. Though the size of grains is almost the same between the undoped and MnCO\(_3\)-doped specimens, the distribution of glass phase of the samples doped with 0.75 wt% MnCO\(_3\) was more extensive than other samples. From the SEM images, it is observed that the MnCO\(_3\) additive can lower the sintering temperature of CTLA ceramics, but dose not enhance the grain growth.

![Figure 5](image)

**Figure 5.** SEM micrographs of CTLA ceramics with CuO additive sintered at 1320°C for 2h (a)0.00wt% CuO (b)0.50wt% CuO (c)0.75wt% CuO (d)1.00wt% CuO; with 0.75wt CuO additive sintered at 1300°C for 2h (e) and sintered at 1340°C for 2h (f); with MnCO\(_3\) addition sintered at 1320°C for 2h (g) 0.50wt% MnCO\(_3\) (h) 0.75wt% MnCO\(_3\) (i) 1.00wt% MnCO\(_3\)**
3.4. Dielectric properties

3.4.1. Effect of the amount of CuO on CTLA ceramics. The dielectric constants of CTLA ceramics with different amounts of CuO additive as functions of their sintering temperatures are displayed in Figure 6. The relationships between \( \varepsilon_r \) values and sintering temperatures reveal the same trend as those between densities and sintering temperatures, because higher density means lower porosity (\( \varepsilon_r =1 \)). The decrease of \( \varepsilon_r \) values could be explained as being due to lower densities as well as to the liquid phase effect. The \( \varepsilon_r \) values of the well-sintered CTLA ceramics range from 43 to 45.

The Q\( \times f \) values of CTLA ceramics with various amounts of CuO additive as functions of their sintering temperatures, are shown in Figure 7. With the increasing of sintering temperature, the Q\( \times f \) values of CTLA ceramics doped with different amounts of CuO increase firstly, after reach the maximal value at a certain temperature, then decrease. The Q\( \times f \) values of CTLA ceramics increase with the increasing amount of CuO additive, after reach the maximum value at the 0.75wt% CuO addition, and then decrease slightly with more addition of CuO. It is expressed that the addition of 0.75wt% CuO would be the most suitable amount for CTLA ceramics.

It has been reported [10] that the microwave dielectric loss is mainly caused not only by the lattice vibrational modes, but also by the pores and the secondary phases. Relative density plays an important role in controlling dielectric loss, as has been shown for other microwave dielectric materials. However, the Q\( \times f \) value has been reported [11] to be independent of the density and the porosity for a theoretical density greater than 90%. Because the secondary phase and charge unbalance are not possible, the grain morphology is suggested to dominate the Q\( \times f \) values of CTLA ceramics with CuO additive.

The grain size of CTLA ceramics with respect to the sintering aid content is critical for understanding the dielectric loss. Grain size is similar for different amounts of CuO additive in this study. However, the Q\( \times f \) values vary dramatically with CuO additive. The Q\( \times f \) value with 0.75wt% CuO addition is much higher than that with either 0.5wt% or 1wt% CuO addition at 1320°C. From Figure 5(b)-(d) it is observed that the grain morphology for 0.75wt% CuO addition is more uniform than that for the 0.5wt% or 1wt% addition. This would reveal reductions in lattice imperfection as well as dielectric loss for the ceramics [10].

The \( \tau_f \) values of CTLA ceramics with different amounts of CuO addition as functions of their sintering temperatures are present in Figure 8. No any significant changing is observed in the \( \tau_f \) value with fixed addition of CuO at different sintering temperature. The \( \tau_f \) value is known as to be related with the composition and the secondary phase of the material. Because CTLA ceramics are temperature stable, and addition of CuO does not cause a secondary phase, the \( \tau_f \) values do not change much in the experiment. With the addition of 0.75wt% CuO, the CTLA ceramics sintered at 1320°C get excellent microwave dielectric properties of an \( \varepsilon_r \) value of 43.51, a Q\( \times f \) value of 32,705 GHz (at 6 GHz), and a \( \tau_f \) value of +9.48 ppm/°C.

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**Figure 6.** Dielectric constants of CTLA ceramics with CuO additives sintering at different temperature

**Figure 7.** Quality factors of CTLA ceramics with CuO additives sintering at different temperature

**Figure 8.** Temperature coefficients of resonant frequency of CTLA ceramics with CuO additives sintering at different temperature
3.4.2. Effect of the amount of MnCO$_3$ on CTLA ceramics. The dielectric constants of CTLA ceramics with different levels of MnCO$_3$ additive of sintering temperature are demonstrated in Figure 9. The relationship between $\varepsilon_r$ values and sintering temperature is the same as that between relative densities and sintering temperature. Those phenomena are attributed to the increase of relative densities which depended on the sintering temperature. Maximal $\varepsilon_r$ values of CTLA ceramics doped and undoped are almost the same, which is about 44.5. Therefore, it suggests that $\varepsilon_r$ values of CTLA ceramics have not significant correlation with the amount of MnCO$_3$ additive. The phenomenon is similar to the CTLA ceramics with different amounts of CuO. The $Q\times f$ values of CTLA ceramics doped with different amounts of MnCO$_3$ as a function of sintering temperature are revealed in Figure 10. With the increasing of sintering temperature, the $Q\times f$ values of CTLA ceramics doped with different amounts of MnCO$_3$ increase firstly, after reach the maximal value at a certain temperature, then decrease. Maximal $Q\times f$ value of CTLA ceramics undoped is 23,241GHz, however, maximal $Q\times f$ values of CTLA ceramics doped with MnCO$_3$ of 0.75wt% is 32,896GHz. The $Q\times f$ values of CTLA ceramics increase with the increasing amount of MnCO$_3$ addition, after reach the maximum value at the 0.75wt% MnCO$_3$ addition. It is expressed that the addition of 0.75wt% MnCO$_3$ would be the most suitable amount for CTLA ceramics. It might be due to variable valence of Mn ion in MnCO$_3$ which decrease effectively the leak loss of conduction current.

The $\tau_f$ values of CTLA ceramics with different amounts of MnCO$_3$ addition as functions of sintering temperature are displayed in Figure 11. Not any significant change is observed in the $\tau_f$ values with fixed MnCO$_3$ addition at different sintering temperature. Because CTLA ceramics are temperature stable, and MnCO$_3$ additions do not cause a secondary phase, the $\tau_f$ values do not change much in the experiment. With 0.75wt% MnCO$_3$ addition, the CTLA ceramics sintered at 1320°C obtain excellent microwave dielectric properties of an $\varepsilon_r$ value of 43.05, a $Q\times f$ value of 32,896GHz (at 6GHz), and a $\tau_f$ value of +10.59ppm/°C.

4. Conclusion
The effects of CuO and MnCO$_3$ additives on the microwave dielectric properties and the microstructures of CTLA ceramics were investigated. CTLA ceramics with proper additions of CuO/MnCO$_3$ could be well sintered to approach 94% theoretical density at 1320°C due to the liquid phase effect. The reduction of the dielectric loss of CTLA ceramics with CuO additive might be dominated by the uniform grain morphology, while the reduction of the dielectric loss of CTLA ceramics with MnCO$_3$ additive might be attributed to variable valence of Mn ion in MnCO$_3$ which decreased effectively the leak loss of conduction current.

CTLA ceramics with the addition of 0.75wt% CuO/MnCO$_3$ sintered at 1320°C for 2h resulted in a $\varepsilon_r$ of 43, a $Q\times f$ value of 32,800 GHz, and a $\tau_f$ value of +10 ppm/°C. Therefore, the sintering
temperature of CTLA ceramics can be lowered effectively with CuO/MnCO$_3$ additive without decreasing the microwave dielectric properties.

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