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# Sintering Behaviors, Microstructure, and Microwave Dielectric Properties of CaTiO<sub>3</sub>–LaAlO<sub>3</sub> Ceramics Using CuO/B<sub>2</sub>O<sub>3</sub> Additions

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**Abstract:** The effect of CuO/B<sub>2</sub>O<sub>3</sub> additions on the sintering behaviors, microstructures, and microwave dielectric properties of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics is investigated. It is found that the sintering temperatures are lowered efficiently from 1600 °C to 1350 °C, as 1 wt % CuO, 1 wt % B<sub>2</sub>O<sub>3</sub>, and 0.5 wt % CuO +0.5 wt % B<sub>2</sub>O<sub>3</sub> are used as the sintering aids due to the appearance of the liquid phase sintering. The microwave dielectric properties of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics with the sintering aid additions are strongly related to the densification and the microstructure of the sintered ceramics. At the sintering temperature of 1300 °C, the 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramic with 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> addition shows the best dielectric properties, including a dielectric constant ( $\varepsilon_r$ ) of 21, approximate quality factor (Q × f) of 22,500 GHz, and a temperature coefficient of the resonant frequency ( $\tau_f$ ) of –3 ppm/°C.

Keywords: microwave; ceramics; density; dielectric properties

# 1. Introduction

Microwave passive communication components can be seen in current communication products, such as in the base station of 5G communication systems or portable mobile phones. Since the size of the microwave passive component determines the dimension of the wireless communication apparatus, the size reduction of the microwave passive components is always an inevitable trend [1]. The microwave materials with high dielectric constants ( $\varepsilon_r$ ), high qualify factor (Q × f) values, and small temperature coefficients of the resonant frequency ( $\tau_f$ ) have been extensively developed in the past 20 years to meet the miniaturization requirement of the circuits [2–4]. To further reduce the circuit size, bandpass filters and antenna duplexers are suitable to implement on the multilayered ceramic. In order to achieve energy-saving goals and fabricate the multilayer microwave devices, microwave dielectric materials with low sintering temperatures and low-melting-point conductors are needed to co-fire [5]. However, many commercial dielectric materials used for high-frequency device applications have high sintering temperatures; thus, they are not well matched with low-temperature sintering processes [2,3]. Microwave sintering or cold-sintering technologies are also reported to further reduce the sintering temperature of the dielectric materials [6,7]; however, the industrial production is still needed to develop.

In past, three methods—chemical processing [8], low-melting glass addition [9,10], and sintering aid addition [11–14]—have been commonly used to reduce the sintering temperature of dielectric ceramics. Chemical processing can lower the sintering temperature by altering the particles sizes of the ceramic powders. However, the processing is typically complex and expensive [8]. Low-melting glass addition is a low cost and easy process. Many of the low temperature sintering ceramics using glass additions have already been investigated. However, low-melting glass addition might reduce the microwave dielectric properties of the ceramics, especially in quality factor due to the many defects [9]. Sintering aid addition is also a cost-effective and simple way to reduce the sintering temperature by providing the liquid phase sintering in some specific aids such as ZnO, Bi<sub>2</sub>O<sub>3</sub>, CuO, B<sub>2</sub>O<sub>3</sub>, or V<sub>2</sub>O<sub>5</sub>.

The LaAlO<sub>3</sub> dielectric ceramic is reported as a phase-stable and low-loss dielectric material, but it has a large negative  $\tau_f$  value of approximately -45 ppm/°C [15]. The dielectric resonator made by LaAlO<sub>3</sub> material with such a high negative  $\tau_f$  produces a large resonant frequency shift when using in the base station operating in a large temperature range. To adjust the temperature coefficient value approaching to zero, an LaAlO<sub>3</sub> material is combined with different perovskite materials such as SrTiO<sub>3</sub> or CaTiO<sub>3</sub> materials with large positive temperature coefficients [16–21]. CaTiO<sub>3</sub> with a large positive  $\tau_f$  value of ~800 ppm/°C is suitable to tune the  $\tau_f$  value of the LaAlO<sub>3</sub> material [18]. With the ratio of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub>, the  $\tau_f$  value can be tuned to around 0 ppm/°C [20]. However, the sintering temperature needed to densify 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics was as high as 1600 °C. It is known that the main effect for liquid phase sintering is that the liquid phase needs to wet the sintered grains and then help grain growth [22]. Since it is cheaper and easier to lower the firing temperature with liquid phase sintering, there is a need to study the effect of liquid phase sintering aids on the sintering and microwave dielectric properties of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics.

In this paper, CuO and  $B_2O_3$  are used as the sintering aids due to the appearance of the liquid phase sintering. The effect of additions of 1 wt % CuO, 1 wt %  $B_2O_3$ , and 0.5 wt % CuO + 0.5 wt %  $B_2O_3$  on the sintering behaviors, microstructures, and microwave dielectric properties of 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics was investigated.

## 2. Experimental Procedure

The starting materials were La<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CaCO<sub>3</sub>, and TiO<sub>2</sub> high-purity oxide powders, which were mixed and ground in distilled water for 12 h in a balling mill with agent balls in relation to the required composition. Mixed powders were dried and then calcined at 1200 °C for 3 h, and then re-milled with different sintering aids for 3 h. In this study, three doping conditions are used to investigate the ability of lowering the sintering temperature, including 1 wt % CuO, 1 wt % B<sub>2</sub>O<sub>3</sub>, and 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub>. After drying, the calcined powder was added with the binder, polyvinyl alcohol (PVA). Pellets with 15 mm diameter that were 5 mm thick were prepared by uniaxial pressing. These pellets were heated at a temperature of 300 °C for 1 h at first to remove the binder. Then, these pellets were sintered at temperatures of 1250–1400 °C for 3 h. Pure 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics disk without addition were also prepared through the similar procedure and sintered at temperatures of 1500–1600 °C for 3 h for the comparison.

The bulk densities of the sintered pellets were measured by the Archimedes method. The theoretical densities (D) for the sintered 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics can be obtained as

$$D = (W_1 + W_2)/(W_1/D_1 + W_2/D_2)$$
(1)

where  $W_1$  and  $W_2$  are the weight percentages of  $0.95LaAlO_3-0.05CaTiO_3$  ceramics and sintering aids in combination, respectively.  $D_1$  and  $D_2$  are the densities of  $0.95LaAlO_3-0.05CaTiO_3$  ceramic and sintering aid in the mixture, respectively. In generally, Equation (1) is only effective when no interaction happened between the dielectric material and the sintering aid.

The crystalline phases of the sintered ceramics were identified by X-ray diffraction patterns (XRD, RIGAKU-2000 X-Ray Diffractometer, Tokyo, Japan). The microstructure of the sintered surface of

ceramics was observed by scanning electron microscopy (SEM, JEOL-JSM-6700F, Tokyo, Japan) and energy dispersive spectra (EDS, JEOL-JSM-6700F, Tokyo, Japan).

The dielectric constant  $\varepsilon_r$  and the quality factor Q at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method improved by Courtney [23,24]. The quality factor is further expressed as Q × f, since it is typically constant in the microwave region. A cylindrical dielectric resonator was positioned between two brass plates connected to the measuring system. A HP8757D network analyzer and a HP8350B sweep oscillator were used in the measurement. The temperature coefficient of resonant frequency ( $\tau_f$ ) at the microwave frequency was measured in the temperature range from 20 °C to 80 °C, and estimated by Equation (2),

$$\tau_f = (f_{80} - f_{20})/(60 \times f_{20}) \times 10^6 \text{ (ppm/°C)}$$
<sup>(2)</sup>

where  $f_{20}$  and  $f_{80}$  are the TE<sub>015</sub> resonant frequency at 20 °C and 80 °C, respectively.

## 3. Results and Discussion

Pure 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics without addition were also prepared and used as the standard reference. The sintered samples without sintering aids have relative theoretical densities of 90% and 95% at the sintering temperature of 1500 °C and 1550 °C, respectively. LaAlO<sub>3</sub> ceramic has approximate dielectric property values of  $\varepsilon_r$  20, Q × f 65,000 GHz, and  $\tau_f$  –50 ppm/°C, and CaTiO<sub>3</sub> ceramic has approximate dielectric properties values of  $\varepsilon_r$  104, Q × f 3600 GHz, and  $\tau_f$  800 ppm/°C. The dielectric properties of the 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramic is suggested to follow the well-known mixing rules [3]:

$$\ln\varepsilon_r = v_1 \ln\varepsilon_1 + v_2 \ln\varepsilon_2 \tag{3}$$

$$Q^{-1} = v_1 Q_1^{-1} + v_2 Q_2^{-1}$$
(4)

$$\tau_f = v_1 \,\tau_{f\,1} + v_2 \,\tau_{f2} \tag{5}$$

where  $v_1$  and  $v_2$  represent the volume fraction of LaAlO<sub>3</sub> and CaTiO<sub>3</sub>, respectively. With the ratio of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub>, it exhibits the approximately dielectric property values of  $\varepsilon_r$  20–22, Q × f 35,000 GHz, and  $\tau_f$  1 ppm/°C.

## 3.1. Microstructure

Figure 1 shows the X-ray patterns of  $0.95LaAlO_3-0.05CaTiO_3$  ceramics sintered at different temperatures with the addition of (a) 1 wt % CuO, (b) 1 wt % B<sub>2</sub>O<sub>3</sub>, and (c) 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub>. It is observed from Figure 1 that LaAlO<sub>3</sub> is the main crystallize phase of the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics. For addition of 1 wt % CuO, as shown in Figure 1a, at the sintering temperature of 1250 °C, LaAlO<sub>3</sub> and the small amount of CaTiO<sub>3</sub> are solid-dissolved together, but the secondary phase CaAl<sub>12</sub>O<sub>19</sub> is still produced. As the sintering temperature rises, the secondary phase gradually disappears. When the sintering temperature is at 1350 °C, the secondary phase completely disappears, and the ceramic is formed as a solid solution.

For additions of 1 wt %  $B_2O_3$  and 0.5 wt % CuO + 0.5 wt %  $B_2O_3$ , the crystallize phases of the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics with different sintering temperatures show similar results. At the sintering temperature of 1250 °C, many secondary phases such as  $La_5Ti_5O_{17}$ ,  $La_4Ti_9O_{24}$ ,  $La_2Ti_2O_7$ , and  $CaAl_4O_7$  exist; even  $LaAlO_3$  and  $CaTiO_3$  are solid-dissolved together. However, the secondary phase disappears rapidly as the sintering temperature rises. The secondary phase almost completely disappears, and the ceramics have formed a solid solution completely at the sintering temperature of 1350 °C.

Figure 2 shows micrographs of  $0.95LaAlO_3-0.05CaTiO_3$  ceramics sintered at different temperature for 3 h with 1 wt % CuO addition. The melting point of the added CuO is as low as about 1026 °C, which is easy to cause a liquid phase sintering for the  $0.95LaAlO_3-0.05CaTiO_3$  ceramics. Moreover, the liquid phase effect would be enhanced by the eutectic of CuO–Cu<sub>2</sub>O–TiO<sub>2</sub> (Cu<sub>3</sub>TiO<sub>4</sub>) at 1070 °C [25].

However, due to an inhomogeneous liquid phase distribution, the growth of crystal grains during high temperature sintering is not homogeneous. At sintering temperatures below 1350 °C, many pores exist. As the sintering temperature rises to 1400 °C, the crystal grain is densely arranged on the ceramic surface. However, the internal structure can be found to have a gap, and it is judged that the dense effect is not good. It is reported that the sintering aids would still exist or evaporate after the liquid phase sintering; thus, EDS analysis is used to identify the elements on the surface of the sintered sample [11]. As shown in Figure 2e, Cu atoms are detected as existing on the grains in the surface after the liquid phase sintering.

Figure 3 shows micrographs of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics sintered at different temperatures for 3 h with 1 wt % B<sub>2</sub>O<sub>3</sub> additions. When the sintering temperature is 1250 °C, the crystal grains dissolve into small particles. As the sintering temperature increases to 1350 °C, the crystal grains grow and gradually become uniform, which leads to more densification. Liquid phase sintering help the growth of crystal grains, and the surface microstructure will be easily covered by the liquid phase [10]. It is resulted that B<sub>2</sub>O<sub>3</sub> belongs to a low melting point material (about 450 °C) and is a well-known liquid promoter. Moreover, the grain-wetting ability of B<sub>2</sub>O<sub>3</sub> addition is better than that of CuO addition in 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics. Moreover, as shown in Figure 3e, the B atom is also detected as existing in the surface of the grain after the liquid phase sintering.

Figure 4 shows micrographs of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics sintered at different temperatures for 3 h with 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> addition. The CuO and B<sub>2</sub>O<sub>3</sub> added in the experiment are all low-melting materials [13,14]. During the sintering temperatures above 1250 °C, liquid phase sintering is clearly observed, since the crystal grains grow non-homogeneously. When the sintering temperature reaches 1300 °C, the pores have all disappeared. The liquid phase sintering is very obvious, and the complete densification is achieved at the sintering temperature of 1300 °C. It is shown that as the sintering temperature exceeds 1350 °C, an excessive liquid phase is generated, and thus the growth of crystal grains is not homogeneous, and the secondary recrystallization is formed, which would affect the performance of the dielectric characteristics. Secondary recrystallization typically occurs when continuous grain growth is inhibited by the present of impurities or the liquid phase, as shown in Figure 4d. It is also identified that Cu and B atoms are both detected as existing in the surface of the grain after liquid phase sintering, as shown in Figure 4e.



(a)

Figure 1. Cont.



(b)

• LaAlO<sub>3</sub>  $\blacktriangle$  La<sub>5</sub>Ti<sub>5</sub>O<sub>17</sub>  $\diamondsuit$  La<sub>4</sub>Ti<sub>9</sub>O<sub>24</sub>

 $\bigcirc$  La<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>  $\square$  CaAl<sub>4</sub>O<sub>7</sub>



<sup>(</sup>c)

**Figure 1.** The X-ray patterns of 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics sintered at different temperatures with the addition of (**a**) 1 wt % CuO, (**b**) 1 wt % B<sub>2</sub>O<sub>3</sub>, and (**c**) 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub>.

Figure 5 shows the grain size of  $0.95LaAlO_3-0.05CaTiO_3$  ceramics as the functions of sintering temperature with different sintering aids. Typically, with the increase of sintering temperature, the surface grain size tends to increase, indicating that high temperature sintering can promote grain growth. It is indicated that the grain size of the ceramics with the addition of CuO is about 0.6–1.2 µm, which is larger than others. However, many pores exist in the sintered ceramics. With B<sub>2</sub>O<sub>3</sub> addition, although the grain is close to dense, the grain growth is still slow due to a small grain size of about 0.6–0.8 µm. With 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> addition, the surface is also dense, but the grain growth is increased slowly due to many small grain sizes. In the excessive liquid phase at a sintering temperature of 1400 °C, the surface grain size could not be estimated.



**Figure 2.** Micrographs of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics sintered at different temperatures for 3 h with 1 wt % CuO addition at (**a**) 1250 °C, (**b**) 1300 °C, (**c**) 1350 °C, (**d**) 1400 °C, and (**e**) energy dispersive spectra (EDS) analysis of surface of the sintered ceramic (**c**).

Figure 6 shows a shrinkage ratio of  $0.95LaAlO_3-0.05CaTiO_3$  ceramics sintered at different temperatures with different additions. The shrinkage ratio is defined as the difference of the sample diameter before and after sintering over the sample diameter before sintering. It is found that the shrinkage ratios of  $0.95LaAlO_3-0.05CaTiO_3$  ceramics are around 4-6%, 12-17% and 13-18% for the additions of 1 wt % CuO, 1 wt % B<sub>2</sub>O<sub>3</sub>, and 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub>, respectively. Although the grain sizes of the sintered sample added with 1 wt % CuO are larger than those added with 1 wt % B<sub>2</sub>O<sub>3</sub> and 0.5 wt % CuO + 0.5 wt % DuO + 0.5 wt % DuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub>, the shrinkage ratios are the worst due to non-homogeneous grain growth and the existence of many pores. At 1350 °C, the shrinkage ratio of the sintered sample reaches the maximum relative value, showing that B<sub>2</sub>O<sub>3</sub> addition helps the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics to shrink and be compact.



**Figure 3.** Micrographs of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics sintered at different temperature for 3 h with 1 wt % B<sub>2</sub>O<sub>3</sub> addition at (a) 1250 °C, (b) 1300 °C, (c) 1350 °C, (d) 1400 °C, and (e) EDS analysis of the surface of the sintered ceramic (c).

For density measurements, the 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics without sintering aid addition were also observed as the standard. The 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramic added with 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> can obtain the measured density of 6.01 g/cm<sup>3</sup>, which is a relative theoretical density of 90%, at the sintering temperature of 1250 °C, and the measured density of 6.05 g/cm<sup>3</sup>, which is a relative theoretical density of 94%, at the sintering temperature above 1300 °C. The 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics added with 1 wt % B<sub>2</sub>O<sub>3</sub> obtain relative theoretical densities of around 80–90% at the sintering temperature of 1300–1400 °C. However, the 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramic added with 1 wt % CuO have relative theoretical densities less than 90% at a sintering temperature of 1400 °C, which is the same finding as that from the shrinkage. It shows that the addition of B<sub>2</sub>O<sub>3</sub> combined with CuO helps the compaction of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics and reduces the sintering temperature by nearly 250 °C, as compared to those without sintering aids.



**Figure 4.** Micrographs of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics sintered at different temperature for 3 h with 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> addition at (**a**) 1250 °C, (**b**) 1300 °C, (**c**) 1350 °C, (**d**) 1400 °C, and (**e**) EDS analysis of surface of the sintered ceramic (**c**).



**Figure 5.** The grain size of 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics as a function of sintering temperature.



**Figure 6.** Shrinkage of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics sintered at different temperatures with different additions.

### 3.2. Dielectric Properties

Figure 7 indicates dielectric constants ( $\varepsilon_r$ ) of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics as the functions of sintering temperature with different additions. In the sintering range, 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics added with 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> have higher dielectric constants of around 19–20.5, which resulted from the full condensation. 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics added with 1 wt % B<sub>2</sub>O<sub>3</sub> have dielectric constants of around 15.8–18.2 due to the lower densification and the excessive secondary phase formation at lower sintering temperatures. The 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics added with 1 wt % CuO have low dielectric constants due to the low density and the excess pores with air phase ( $\varepsilon_r = 1$ ) [2].



**Figure 7.** Dielectric constants of 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics as the functions of sintering temperatures with different additions.

Figure 8 indicates the quality factor  $Q \times f$  values of  $0.95LaAlO_3-0.05CaTiO_3$  ceramics as the functions of the sintering temperature with different additions. It is known that the microwave dielectric loss is simultaneously affected by many factors, which are mainly caused not only by densification, pores, and grain sizes/boundaries, and but also by the lattice secondary phases and vibration modes [8]. It seems that the relative theoretical density and pores are important factors in controlling the dielectric loss. As shown in Figure 8, the  $0.95LaAlO_3-0.05CaTiO_3$  ceramic added with 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> has a higher Q × f value of around 22,500 GHz at the sintering temperature of 1300 °C, which is

near the Q × f value of the 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramic without sintered aid sintered at 1550 °C. After the sintering temperature exceeds 1350 °C, the Q × f value decreases, which is presumed to be caused by the excessive liquid phase of the ceramic. The 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics added with 1 wt % B<sub>2</sub>O<sub>3</sub> have Q × f values of around 1000–12,000 GHz, which is affected by the low densification [3]. The 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics added with 1 wt % CuO have low densities and contain too much pores, resulting in the worst performance of Q × f values.



**Figure 8.**  $Q \times f$  values of 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics as the functions of sintering temperature with different additions.

Figure 9 indicates  $\tau_f$  values of 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics as the functions of sintering temperature with different additions. The  $\tau_f$  values of 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics added with 1 wt % CuO and 1 wt % B<sub>2</sub>O<sub>3</sub> have a negative value and a positive value, respectively. It is found that the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics added with 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> have an acceptable temperature coefficient of resonant frequency ( $\tau_f$ ) approaching zero value. Generally, the temperature coefficient of resonant frequency ( $\tau_f$ ) is dependent on the composition and the existing phase in the ceramics [10]. In this study, the sintered ceramic with CuO addition has a negative temperature coefficient, while that with B<sub>2</sub>O<sub>3</sub> addition has a positive temperature coefficient. Since the ratio of CaTiO<sub>3</sub> to LaAlO<sub>3</sub> is also appropriate, a system with a temperature coefficient approaching zero can be obtained.



**Figure 9.**  $\tau_f$  values of 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics as the functions of sintering temperature with different additions.

# 4. Conclusions

LaAlO<sub>3</sub> is a quite potential microwave dielectric material with a dielectric constant ( $\varepsilon_r$ ) of 23, a quality factor (Q × f) value of 65,000 GHz, and a negative temperature coefficient of temperature ( $\tau_f$ ) of -44 ppm/°C. For mixing CaTiO<sub>3</sub> ceramic as compensation for the temperature coefficient of resonant frequency, 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramic is used in this study. In order to reduce the sintering temperature, CuO and B<sub>2</sub>O<sub>3</sub> sintering aids for liquid phase sintering are added to the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramic to help grain growth, to increase the density, as well as to obtain acceptable quality factors of the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics.

The effects of the liquid phase sintering aids added to the  $0.95LaAlO_3-0.05CaTiO_3$  ceramic are summarized as follows.

- 1. For the addition of 1 wt % CuO to the 0.95LaAlO<sub>3</sub>–0.05CaTiO<sub>3</sub> ceramics, the effect is the worst. When the sintering temperature is 1400 °C, the dielectric constant ( $\epsilon_r$ ) is about 16, the highest quality factor (Q × f) value is about 7500 GHz, and the temperature coefficient of resonant frequency ( $\tau_f$ ) is about –11 ppm/°C.
- 2. For the addition of 1 wt % B<sub>2</sub>O<sub>3</sub> to the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics, the sintering temperature is lowered to 1400 °C, the electrical constant ( $\varepsilon_r$ ) is about 18, the highest quality factor (Q × f) value is about 10,000 GHz and the temperature coefficient of resonant frequency ( $\tau_f$ ) is about -5 ppm/°C.
- 3. For the addition of 0.5 wt % CuO + 0.5 wt % B<sub>2</sub>O<sub>3</sub> to the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramics, its sintering temperature can be reduced to 1300 °C (about 250 °C reduction, as compared to the same relative theoretic density of the 0.95LaAlO<sub>3</sub>-0.05CaTiO<sub>3</sub> ceramic without a sintering aid), the dielectric constant ( $\varepsilon_r$ ) is about 21, the highest quality factor (Q × f) value is 22,500 GHz, and the temperature coefficient of the resonant frequency ( $\tau_f$ ) is about -3 ppm/°C.

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# References

- 1. Sebastian, M.T. Dielectric Materials for Wireless Communication; Elsevier: Amsterdam, the Netherland, 2008.
- 2. Kagata, H.; Kato, J. Dielectric Properties of Ca-Based Complex Perovskite at Microwave Frequencies. *Jpn. J. Appl. Phys.* **1994**, *33*, 5463–5465. [CrossRef]
- 3. Huang, C.C.; Yang, R.Y.; Weng, M.H. Dielectric properties of Ca(Mg,Nb)O<sub>3</sub>-CaTiO<sub>3</sub> solid solution at microwave frequency. *Jpn. J. Appl. Phys.* **2000**, *39*, 6608–6611. [CrossRef]
- 4. Huang, C.L.; Weng, M.H. Improved high Q value of MgTiO<sub>3</sub>–CaTiO<sub>3</sub> microwave dielectric ceramics at low sintering temperature. *Mat. Res. Bull.* **2000**, *36*, 2741–2750. [CrossRef]
- Pang, L.; Zhou, D.; Wang, D.; Zhao, J.; Liu, W.; Yue, Z.; Reaney, I.M. Temperature stable K<sub>0.5</sub>(Nd<sub>1-x</sub>Bi<sub>x</sub>)<sub>0.5</sub>MoO<sub>4</sub> microwave dielectrics ceramics with ultra-low sintering temperature. *J. Am. Ceram. Soc.* 2018, 101, 1806–1810. [CrossRef]
- 6. Tian, L.J.; Wng, N.H.; Shen, C.Y. Effect of Microwave Sintering on the Properties of 0.95 (Ca<sub>0.88</sub>Sr<sub>0.12</sub>)TiO<sub>3</sub>-0.05 (Bi<sub>0.5</sub>Na<sub>0.5</sub>)TiO<sub>3</sub> Ceramics. *Materials* **2019**, *12*, 803. [CrossRef]
- Wang, D.; Zhang, S.; Zhou, D.; Song, K.; Feteira, A.; Vardaxoglou, Y.; Whittow, W.; Cadman, D.; Reaney, I.M. Temperature Stable Cold Sintered (Bi<sub>0.95</sub>Li<sub>0.05</sub>) (V<sub>0.9</sub>Mo<sub>0.1</sub>)O<sub>4</sub>-Na<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub> microwave dielectric composites. *Materials* 2019, *12*, 1370. [CrossRef]
- Weng, M.H.; Liang, T.J.; Huang, C.L. Lowering of sintering temperature and microwave dielectric properties of BaTi<sub>4</sub>O<sub>9</sub> ceramics prepared by the polymeric precursor method. *J. Eur. Ceram. Soc.* 2002, 22, 1693–1698. [CrossRef]

- Hsian, H.I.; Chen, C.C.; Yang, S.Y. Microwave dielectric properties of Ca<sub>0.7</sub>Nd<sub>0.2</sub>TiO<sub>3</sub> ceramic-filled CaO–B<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> glass for LTCC applications. *J. Adv. Ceram.* 2019, *8*, 345–351. [CrossRef]
- 10. Hunag, C.L.; Weng, M.H.; Lion, C.C.; Wu, C.C. Low temperature sintering and microwave dielectric ceramics of Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub> using glass additions. *Mat. Res. Bull.* **2000**, *35*, 2445–2456. [CrossRef]
- 11. Huang, C.L.; Weng, M.H.; Chen, H.L. Effects of additives on microstructures and microwave dielectric properties of (Zr, Sn)TiO<sub>4</sub> ceramics. *Mat. Chem. Phys.* **2001**, *71*, 17–22. [CrossRef]
- Kim, M.H.; Jeong, Y.H.; Nahm, S.; Kim, H.T.; Lee, H.J. Effect of B<sub>2</sub>O<sub>3</sub> and CuO additives on the sintering temperature and microwave dielectric properties of Ba(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub> ceramics. *J. Eur. Ceram. Soc.* 2006, 26, 2139–2142. [CrossRef]
- Lim, J.B.; Nahm, S.; Kim, H.T.; Kim, J.H.; Park, J.H.; Lee, H. Effect of B<sub>2</sub>O<sub>3</sub> and CuO on the sintering temperature and microwave dielectric properties of the BaTi<sub>4</sub>O<sub>9</sub> ceramics. *J. Electroceramics Ceram.* 2006, 17, 2–4. [CrossRef]
- 14. Yim, D.K.; Kim, J.R.; Kim, D.W.; Hong, K.S. Microwave dielectric properties and low-temperature sintering of Ba<sub>3</sub>Ti<sub>4</sub>Nb<sub>4</sub>O<sub>21</sub> ceramics with B<sub>2</sub>O<sub>3</sub> and CuO additions. *J. Eur. Ceram. Soc.* **2007**, *27*, 3053–3057. [CrossRef]
- 15. Moon, J.H.; Park, H.S.; Lee, K.T.; Choi, J.H.; Yeo, D.H.; Yoon, S.J.; Kim, H.J. Microwave dielectric properties of the (1-x)La<sub>2/3</sub>TiO<sub>3</sub>-xLaAlO<sub>3</sub> system. *Jpn. J. Appl. Phys.* **1997**, *36*, 6814–6817. [CrossRef]
- Sun, P.H.; Nakamira, T.; Shn, Y.J.; Inaguma, Y.; Itoh, M.; Kitamura, T. Dielectric behavior of (1-x)LaAlO<sub>3</sub>-xSrTiO<sub>3</sub> solid solution system at microwave frequencies. *Jpn. J. Appl. Phys.* **1998**, *37*, 5625–5629. [CrossRef]
- 17. Cho, S.Y.; Hong, K.S.; Ko, K.H. Mixture-like behavior in microwave dielectric propeties of the (1-x)LaAlO<sub>3</sub>-xSrTiO<sub>3</sub> System. *Mat. Re. Bull.* **1999**, *34*, 511–516. [CrossRef]
- 18. Jiang, J.; Fang, D.; Lu, C.; Dou, Z.; Wang, G.; Zhang, F.; Zhang, T. Solid-state reaction mechanism and microwave dielectric properties of CaTiO<sub>3</sub>–LaAlO<sub>3</sub> ceramics. *J. Alloys Compd.* **2015**, *638*, 443–447. [CrossRef]
- Vidmar, M.; Golobic, A.; Meden, A.; Suvorov, D.; Skapin, S.D. Sub-solidus phase relations and a structure determination of new phases in the CaO–La<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system. *J. Eur. Ceram. Soc.* 2015, *35*, 2801–2814. [CrossRef]
- 20. Dou, Z.M.; Wang, G.; Jiang, J.; Zhang, F.; Zhang, T.J. Understanding microwave dielectric properties of (1–x) CaTiO<sub>3</sub>–xLaAlO<sub>3</sub> ceramics in terms of A/B-site ionic-parameters. *J. Adv. Ceram.* **2017**, *6*, 20–26. [CrossRef]
- 21. Eteira, A.; Sinclair, D.C.; Lanagan, M.T. Structure and microwave dielectric properties of Ca<sub>1-x</sub>Y <sub>x</sub>Ti<sub>1-x</sub>Al <sub>x</sub>O<sub>3</sub> (CYTA) ceramics. *J. Mat. Res.* **2005**, *20*, 2391–2399.
- 22. Marison, J.E.; Hsueh, C.H.; Evans, A.G. Liquid phase sintering of ceramics. J. Am. Ceram. Soc. 1987, 70, 708–713. [CrossRef]
- 23. Hakkit, B.W.; Coleman, P.D. A dielectric resonator method of measuring inductive capacities in the millimeter range. *IEEE Trans. Microw. Theory Tech.* **1960**, *8*, 402–410. [CrossRef]
- 24. Courtney, W.E. Analysis and evaluation of a method of measuring the complex permittivity and permeability microwave insulators. *IEEE Trans. Microw. Theory Tech.* **1970**, *18*, 476–485. [CrossRef]
- 25. Huang, C.L.; Weng, M.H. Liquid phase sintering of (Zr, Sn)TiO<sub>4</sub> microwave dielectric ceramics. *Mat. Res. Bull.* **2000**, *35*, 1881–1888. [CrossRef]



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