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Low-temperature firing and microwave dielectric properties of $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ ceramics with V_2O_5 addition

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Abstract

The sintering behaviors and microwave dielectric properties of the $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ (abbreviated CLST) ceramics with different amounts of V_2O_5 addition had been investigated in this paper. The sintering temperature of the CLST ceramic had been efficiently decreased by nearly 100 °C. No secondary phase was observed in the CLST ceramics and complete solid solution of the complex perovskite phase was confirmed. The CLST ceramics with small amounts of V_2O_5 addition could be well sintered at 1200 °C for 3 h without much degradation in the microwave dielectric properties. Especially, the 0.75 wt.% V_2O_5-doped ceramics sintered at 1200 °C for 3 h have optimum microwave dielectric properties of Kr = 100.4, $Q\times f$ = 5600 GHz, and TCF = 7 ppm/°C. Obviously, V_2O_5 could be a suitable sintering aid that improves densification and microwave dielectric properties of the CLST ceramics.

Keywords: Dielectric properties; Perovskites; Sintering; V_2O_5; Functional applications

1. Introduction

Recently, there has been rapid development in communication equipment, such as portable and mobile phones. A microwave dielectric filter, which is one of the key components in this equipment, must have small size, low loss and high stability of resonant frequency. To achieve this, materials with a high dielectric constant (Kr) are required. A high Q value and a near zero temperature coefficient of the resonant frequency (TCF) in the materials are also important factors.

The $CaO–Li_2O–Sm_2O_3–TiO_2$ system which was made by combining $(Li_{1/2}Sm_{1/2})TiO_3$ and $(Ca_{1-x}Sm_{2x/3})TiO_3$ ($x < 0.6$) usually exhibits a perovskite (ABO_3) type structure and has a high Kr, a high Q value and good temperature stability for resonant frequency changes in the microwave region. It has attracted great interests since it was first reported by Ezaki et al.[1] Studies on this system up to now are mainly concentrated on the optimization of microwave dielectric properties. Chen et al.[2] found that sintered $CaO–Li_2O–Sm_2O_3–TiO_2$ (16:9:12:63) at 1325 °C for 3 h showed microwave dielectric properties: Kr = 104.1, $Q\times f$ = 4320 GHz, and TCF = 13.2 ppm/°C. Yoon et al.[3] presented that $(Ca_{0.275}Sm_{0.4}Li_{0.25})(Ti_{1-x}Mn_x)O_3 (0 < x < 5\,\text{mol\%})$ ceramic with the substitution of 1.0 mol% MnO_2 showed the dielectric constant of 97.9, $Q\times f$ value of 6400 and TCF of −10.7 ppm/°C. Huang et al.[4] reported that $CaO–BaO–Li_2O–Sm_2O_3–Nd_2O_3–TiO_2$ (14:4:8:10:2:63) sintered at 1350 °C for 3 h have excellent dielectric properties of Kr = 103, $Q\times f$ = 7200 and TCF = 2 ppm/°C. Yoon et al.[5] gave the result that Sm content in the $(1-y)Ca_{2/5}Sm_{2/5}TiO_3–yLi_{1/2}Sm_{1/2}TiO_3$ sintered at 1300 °C for 3 h affects its dielectric properties and optimum dielectric properties of Kr = 95.5 and $Q\times f$ value = 7200 GHz and TCF = 0 ppm/°C were obtained when x is equal to 0.33. Excellent dielectric properties of Kr = 123 and $Q\times f$ value = 4150 GHz and TCF = 10.8 ppm/°C were obtained with a composition of $CaO:SrO:Li_2O:Sm_2O_3:Nd_2O_3:TiO_2$ = 15:1:9:6:6:63 (molar ratio) in $CaO–SrO–Li_2O–Sm_2O_3–Nd_2O_3–TiO_2$ system sintered at 1400 °C.[6] As mentioned above, these $CaO–Li_2O–Sm_2O_3–TiO_2$-based ceramics usually should be sintered at temperatures above 1300 °C, which are too high in practical applications. Therefore, it is important

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to lower their sintering temperatures without deterioration of dielectric properties. Although low temperature sintering with sintering aids has been successfully achieved in several other microwave dielectric systems, such as $(Ca_{1-x}Mg_x)SiO_3$, $LiNb_{0.6}Ti_{0.5}O_3$ and $Ba_3Ti_4Nb_4O_{21}$,[7–9] low temperature firing of $CaO–Li_2O–Sm_2O_3–TiO_2$ system is rarely reported. Only the effect of $B_2O_3–Li_2O$ on the sintering behavior and the microwave dielectric properties of $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ ceramics was reported.[10] The sintering temperature of the specimens with $B_2O_3–Li_2O$ addition was reduced to 1200 °C and optimum microwave dielectric properties obtained were Kr of 98.7, $Q \times f$ value of 5930, and TCF of −3.7 ppm/°C. In literature, V_2O_5 was suggested to be one of promising sintering aids for the densification at relatively low sintering temperatures. For example, the addition of V_2O_5 can effectively lower the sintering temperature of $5Li_2O–Nb_2O_5–5TiO_2$ to 900 °C, $Li_{1+x-y}Nb_{1-x-3y}Ti_{x+4y}O_3$ to 900 °C and $5Li_2O–0.583Nb_2O_5–3.248TiO_2$ to 920 °C.[11–13] However, the influence of V_2O_5 addition on the $CaO–Li_2O–Sm_2O_3–TiO_2$ ceramic has not been reported in our concerned literatures. In this paper, the effects of V_2O_5 content on sintering temperature and microwave dielectric properties of $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ (abbreviated CLST) ceramics were investigated.

2. Experimental

Specimens of CLST ceramics were synthesized by conventional mixed-oxide routes from high-purity oxide powders (>99%): $CaCO_3$, Li_2CO_3, Sm_2O_3 and TiO_2. Proportionate amounts of the above raw materials (16:9:12:63 by mole) were mixed in ethanol medium using ZrO_2 balls for 24 h. The mixtures were dried and calcined in air at 1050 °C for 3 h to form CLST phase. Different amounts of V_2O_5 were individually added in the calcined powder and remilled for 8 h. After drying and sieving, pellets with 10.5 mm in diameter were uniaxially pressed under a pressure of 120 MPa. The undoped pellets were subsequently sintered at temperature of 1300 °C and the V_2O_5-containing pellets were sintered at temperature of 1100–1250 °C for 3 h.

The densities of the sintered ceramics were measured by Archimedes' method. Crystalline phases of the specimens were identified by X-ray powder diffraction patterns (XRD, *Philips X'part Pro* MPC, *Netherlands*, Cu Kα_1). Microstructures of the specimens were studied by scanning electron microscopy (SEM, Jeol, JSM5610LV, Japan). The relative dielectric constants Kr and the quality-factor $Q \times f$ values at microwave frequency were measured with a HP8720ES network analyzer using the post-resonant method developed by Hakki and Coleman.[14] The temperature coefficient of the resonant frequency (TCF) was measured in the temperature range from −20 to 80 °C, and calculated by the following equation:

$$\mathrm{TCF} = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

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

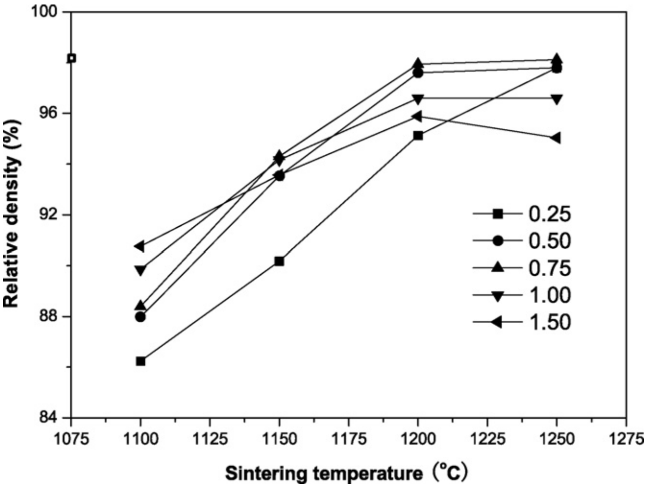

Fig. 1. Relative densities of the $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ ceramics with different amounts of V_2O_5 addition versus sintering temperature.

3. Results and discussion

3.1. Sintering behavior

Fig. 1 shows the relative densities of the ceramics with the addition of 0.25–1.50 wt.% V_2O_5 as a function of sintering temperature from 1100 to 1250 °C for 3 h. The relative densities of the CLST ceramics first increase with increasing sintering temperature, and then almost saturate at 1200–1250 °C. In addition, it could be observed that the relative densities of the 0.50 and 0.75 wt.% V_2O_5-doped ceramics sintered at above 1200 °C were almost the same as that of the undoped CLST ceramic sintered at 1300 °C (98.1% of calculated theoretical density), as is shown on the vertical axis in Fig. 1. Obviously, after adding V_2O_5, the sintering temperature of the CLST ceramic had been efficiently decreased by nearly 100 °C. The highest density could be obtained for the 0.75 wt.% V_2O_5-doped ceramic sin-

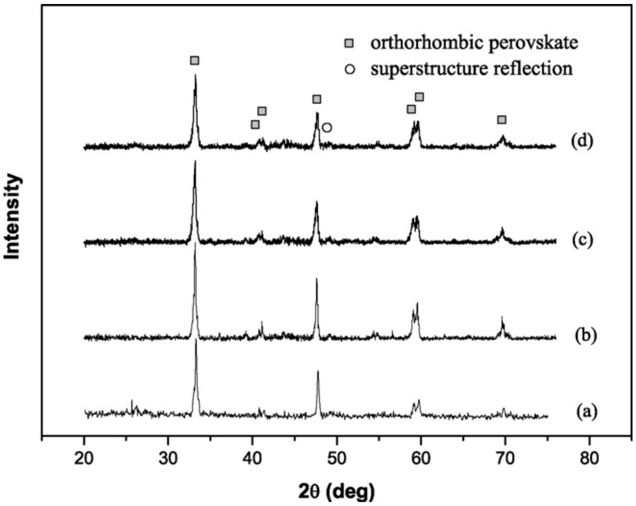

Fig. 2. X-ray diffraction patterns of (a) $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ (CLST) powder calcined at 1050 °C for 3 h, (b) the undoped CLST ceramics sintered at 1300 °C for 3 h, and the CLST ceramics sintered at 1200 °C for 3 h with (c) 0.75 wt.%, (d) 1.5 wt.% V_2O_5 addition.

tered at 1200 °C, and the relative densities of the V_2O_5-doped CLST ceramics decreased as the V_2O_5 contents were further increased, which means ≥ 1.00 wt.% V_2O_5 addition is obviously overweighed to the CLST ceramic.

3.2. Phase composition and microstructure

The XRD patterns of (a) $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ (CLST) powder calcined at 1050 °C for 3 h, (b) the undoped CLST ceramics sintered at 1300 °C for 3 h, and the CLST ceramics sintered at 1200 °C for 3 h with (c) 0.75 wt.%, (d) 1.5 wt.% V_2O_5 addition are illustrated in Fig. 2. It can be seen that the CLST powder calcined at 1050 °C for 3 h exhibited an orthorhombic perovskite structure. No secondary phase was observed in V_2O_5-doped CLST ceramic specimens and complete solid solution of the complex perovskite phase was confirmed, which indicates that V_2O_5 addition has no effect on the phase composition of CLST ceramics. In addition, the slight superstructure reflection lines were also observed at about $2\theta = 49°$ due to the ordering of Li^+ and Sm^{3+} ions and A-site vacancies along the c-axis, which is in accordance with Yoon's results.[10]

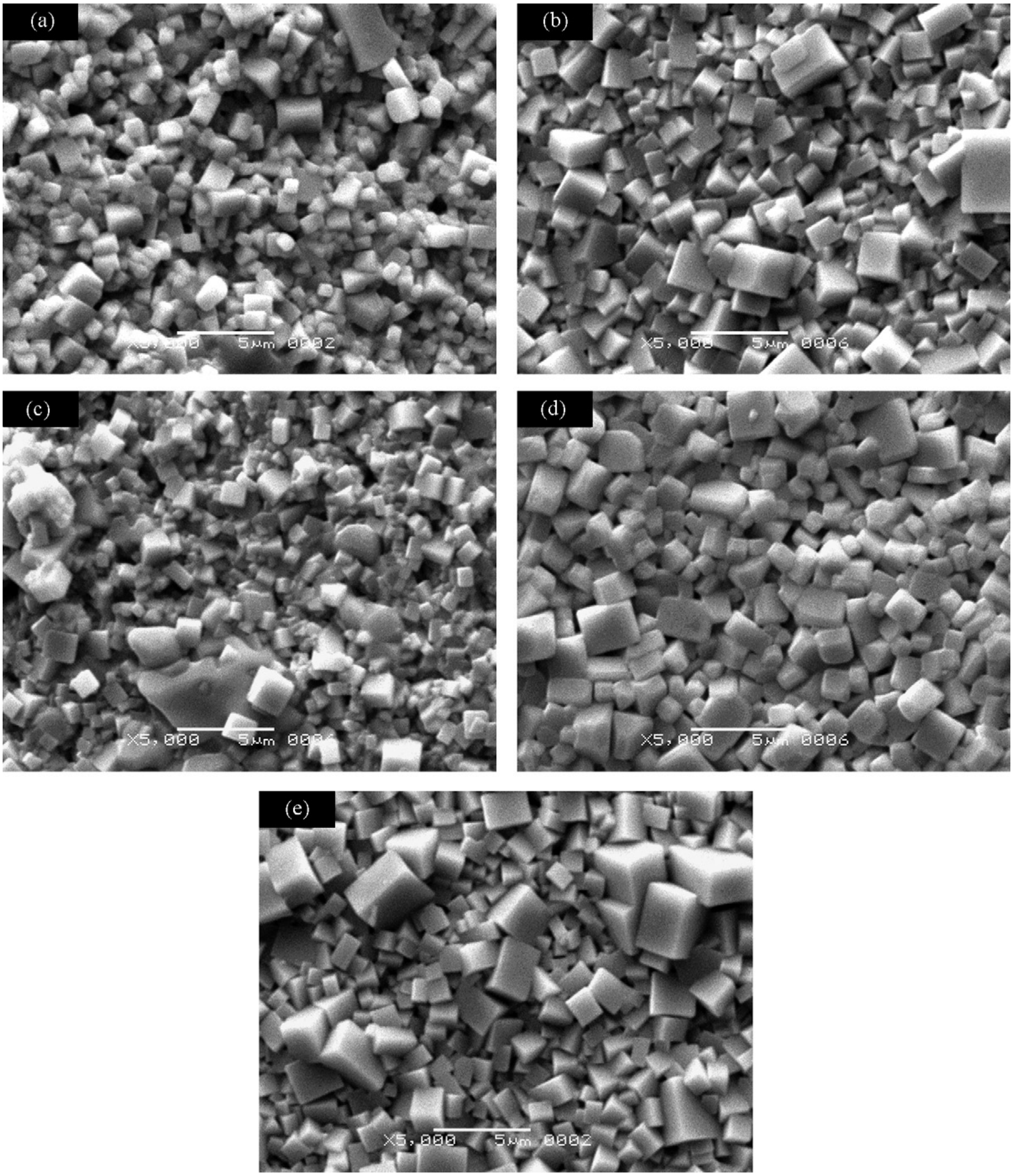

Fig. 3. Scanning electron microscope photographs of the $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ (CLST) ceramics sintered at 1200 °C for 3 h with (a) 0.25 wt.%, (b) 0.75 wt.%, (c) 1.5 wt.% V_2O_5 addition, and (d) micrograph of the undoped CLST ceramics sintered at 1300 °C for 3 h and (e) that of 1.5 wt.% V_2O_5-doped CLST ceramic sintered at 1200 °C for 4 h.

The microstructure photographs of CLST ceramics doped with (a) 0.25 wt.%, (b) 0.75 wt.% and (c) 1.5 wt.% V_2O_5 sintered at 1200 °C for 3 h and that of the undoped CLST ceramic sintered at 1300 °C for 3 h (d) are illustrated in Fig. 3. It can be seen that the grain sizes of the specimens with different amounts V_2O_5 sintered at 1200 °C are similar and a small number of large grains occurs, which means that the V_2O_5 content has some influences on the grain growth. Many pores could be found for the undoped and 0.25 wt.% V_2O_5-doped specimens, in accordance with the lower relative densities in Fig. 1, which indicates 0.25 wt.% V_2O_5 is not enough for densifying the ceramics efficiently at that low sintering temperature. In agreement with the density curve, the dense microstructure had been obtained for the ceramic doped with 0.75 wt.% V_2O_5. More amount of V_2O_5 addition to the CLST ceramics resulted in an increase of porosity due to exaggerated grain growth promoted by overweighed V_2O_5 at 1200 °C. This has been verified by comparing the micrograph of 1.5 wt.% V_2O_5-doped CLST ceramic sintered at 1200 °C for 3 h with that of specimen sintered for 4 h as is shown in Fig. 3(c) and (e).

3.3. Dielectric properties

Fig. 4 presents the dielectric properties of V_2O_5-containing CLST ceramics sintered at 1200 °C for 3 h as a function of V_2O_5 contents. As is shown in Fig. 4(a), the Kr values of these specimens depend on the amount of V_2O_5 addition, which is very similar to that of the relative densities (Fig. 4(d)). Generally, the relative densities of the sintered ceramics determine, to some extent, the dielectric constant of the sintered ceramics, due to the low Kr value of pores (∼1.0). The maximum of Kr value of CLST ceramics could be obtained with 0.75 wt.% V_2O_5 additions due to the dense microstructure (Fig. 3(b)) resulting from V_2O_5 addition.

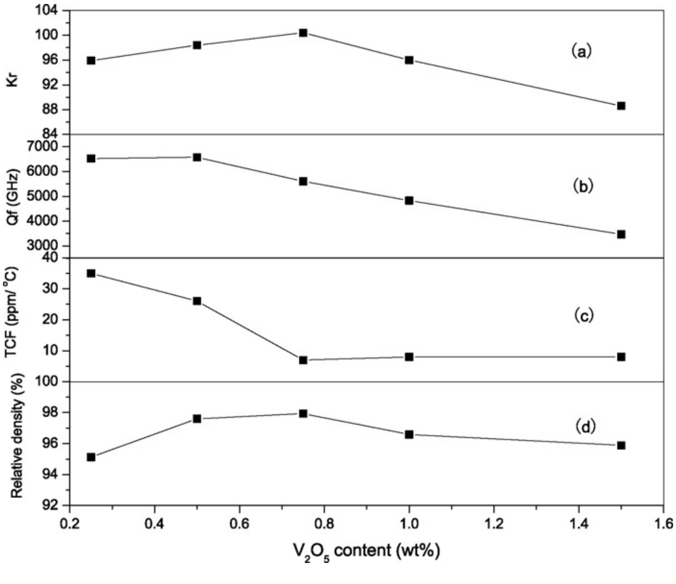

Fig. 4. (a) Dielectric constant values, (b) quality-factor values, (c) the temperature coefficients of resonant frequency and (d) relative densities of the $16CaO–9Li_2O–12Sm_2O_3–63TiO_2$ (CLST) ceramics as a function of the amount of V_2O_5 addition.

The $Q \times f$ values of V_2O_5-doped CLST ceramics as a function of V_2O_5 contents were illustrated in Fig. 4(b). It could be seen that the $Q \times f$ values of V_2O_5-containing specimens increase slightly with the increment of V_2O_5 up to 0.5 wt.%, and then decrease rapidly for further V_2O_5 addition. It is well-known that the microwave dielectric loss includes not only intrinsic losses that are mainly caused by the lattice vibration modes but also extrinsic losses dominated by densification/porosity, the secondary phases, grain sizes and oxygen vacancies, etc.[15] Comparing Fig. 4(d) with (b), the decrease of $Q \times f$ in V_2O_5-doped CLST ceramic when V_2O_5 content was more than 0.75 wt.% might be explained by the decrease of relative density due to the exaggerated grain growth promoted by overweighed V_2O_5. Another probable explanation of this decrease may be the localization of excess V_2O_5 or its derivatives at the boundaries although it has not been observed in our present microstructure. It also could be found that the 0.5 wt.% V_2O_5-doped CLST ceramic possessed the highest $Q \times f$ value, while the relative density was less than that of 0.75 wt.% V_2O_5-doped specimen. It seems to be difficult to explain this result, which needs further study.

Fig. 4(c) shows the TCF values of the CLST ceramics sintered at 1200 °C for 3 h as a function of V_2O_5 content. From Fig. 4(c), it can be observed that the TCF values decrease dramatically with the V_2O_5 addition up to 0.75 wt.%, and then increase slightly for further V_2O_5 addition. The minimum TCF value of the V_2O_5-containing ceramic specimens is 7 ppm/°C.

It has been reported that multi-component oxides are more effective than single component oxides to reduce the sintering temperature of microwave dielectric ceramics without obvious deterioration in microwave dielectric properties.[16–19] As far as $CaO–Li_2O–Sm_2O_3–TiO_2$ microwave dielectric ceramics are concerned, low-temperature firing of one of the stoichiometric $CaO–Li_2O–Sm_2O_3–TiO_2$ microwave dielectric ceramics such as $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ ceramic was realized with $B_2O_3–Li_2O$ addition.[10] The $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ system doped with 0.5 wt.% $B_2O_3–Li_2O$ sintered at 1200 °C for 3 h showed good microwave dielectric properties as high as those of pure $(Ca_{0.275}Sm_{0.4}Li_{0.25})TiO_3$ sintered at 1300 °C. In this paper, dense microstructure and good microwave dielectric properties were also achieved in the CLST ceramic, another nonstoichiometric composition of $CaO–Li_2O–Sm_2O_3–TiO_2$ system, sintered at 1200 °C for 3 h by only adding a single component oxide V_2O_5. The optimum microwave dielectric properties with Kr = 100.4, $Q \times f = 5600$ GHz, TCF = 7 ppm/°C were obtained for 0.75 wt.% V_2O_5-doped CLST ceramics sintering at 1200 °C for 3 h. In order to further lowering the sintering temperature of the CLST system, the effects of V_2O_5-based multi-component oxides addition on CLST ceramics are under investigation.

4. Conclusions

The sintering behaviors and microwave dielectric properties of the CLST ceramics with different amounts of V_2O_5 addition had been investigated in this paper. The CLST ceramics with small amounts of V_2O_5 addition could be well sintered at 1200 °C without much degradation in the microwave dielectric properties. Especially, the 0.75wt.% V_2O_5-doped ceramics sintered at 1200 °C for 3 h have optimum microwave dielectric properties of Kr = 100.4, $Q \times f = 5600$ GHz, and TCF = 7 ppm/°C. Obviously, V_2O_5 could be a suitable sintering aid that improves densification and microwave dielectric properties of the CLST ceramics.

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