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Microwave dielectric properties of $CaWO_4$–Li_2TiO_3 ceramics added with LBSCA glass for LTCC applications

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ABSTRACT

In this work, $0.86CaWO_4$–$0.14Li_2TiO_3$ ceramics were prepared via a traditional solid-state process. The effects of Li_2O–B_2O_3–SiO_2–CaO–Al_2O_3 (LBSCA) addition on the phase formation, sintering character, microstructure and microwave dielectric properties of the ceramics were investigated. A small amount of LBSCA addition could effectively lower the sintering temperature of the ceramics. X-ray diffraction analysis revealed that $CaWO_4$ and Li_2TiO_3 phases coexisted without producing any other crystal phases in the sintered ceramics. The dielectric constant and *Qf* values were related to the amount of LBSCA addition and sintering temperatures. All specimens could obtain near-zero temperature coefficient (τ_f) values through the compensation of the positive τ_f of Li_2TiO_3 and the negative τ_f of $CaWO_4$. The $0.86CaWO_4$–$0.14Li_2TiO_3$ ceramic with 0.5 wt% LBSCA addition and sintered at 900 °C for 3 h exhibited excellent microwave dielectric properties of $\varepsilon_r = 12.43$, $Qf = 76{,}000$ GHz and $\tau_f = -2.9$ ppm/°C.

1. Introduction

The rapid development of wireless communication has created a high demand for microwave ceramic components. To improve the performances and realise the miniaturisation and integration of microwave devices, many studies have investigated the low temperature co-fired ceramic (LTCC) technology. Given its high conductivity and low cost, silver (Ag) has been widely used as internal electrodes in LTCC devices [1–5]. However, given that the melting temperature of Ag is around 961 °C, the typical sintering temperature of LTCC materials must be decreased to around 900 °C or lower [6,7]. Low melting glass additions are often used as sintering aids in LTCC materials. However, inappropriate or excessive glass additions lead to either high microwave dielectric loss or crack formation during soldering, especially when the amount of glass doping exceeds 5 wt% [8]. Therefore, a proper sintering aid must be used to achieve high-performance LTCC materials. Furthermore, the small τ_f of LTCC materials is also important in obtaining stable LTCC microwave components.

$CaWO_4$ is amongst the most promising dielectric ceramics because of its favourable microwave dielectric properties of $\varepsilon_r \approx 10$, high *Qf* value($\approx 75{,}000$ GHz), and $\tau_f \approx -25$ ppm/°C when sintered at 1100 °C [9–11]. To lower the sintering temperature of $CaWO_4$, Zhu Zhang et al. investigated the effects of Li_2WO_4 on the microwave dielectric properties of $CaWO_4$ and reported its corresponding properties when sintered at 900 °C: $\varepsilon_r = 9.002$; $Qf = 117{,}600$ GHz; $\tau_f = -55$ ppm/°C [9]. However, $CaWO_4$–Li_2WO_4 ceramics have very large negative τ_f values, thereby limiting their applications in LTCC technology. Li_2TiO_3 has a relatively low sintering temperature, excellent microwave dielectric properties and positive τ_f ($\varepsilon_r \approx 23.29$, $Qf = 15{,}000$ GHz, $\tau_f = 35.05$ ppm/°C) [12–15]. A near-zero τ_f may be realised by compounding the proper contents of $CaWO_4$ and Li_2TiO_3 together. However, the sintering temperatures of $CaWO_4$–Li_2TiO_3 compound ceramics still exceed the LTCC technology requirements. Therefore, an appropriate sintering aid must be used to lower the sintering temperature of $CaWO_4$–Li_2TiO_3 ceramics without degrading the microwave dielectric properties.

In this work, Li_2O–B_2O_3–SiO_2–CaO–Al_2O_3 (LBSCA) glass was used as a sintering aid to lower the sintering temperature of $CaWO_4$–Li_2TiO_3 compound ceramics. The influences of LBSCA addition on the sintering behaviour, microstructure and microwave dielectric properties of the ceramics were investigated and discussed.

2. Experimental procedure

High-purity WO_3 (99%), $CaCO_3$ (99.9%), Li_2CO_3 (99%) and TiO_2 (99.5%) were used as starting materials. $CaWO_4$ powders were produced by ball-milling WO_3 and $CaCO_3$ in a 1:1 M ratio; they

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were then dried and calcined at 850 °C. Li_2TiO_3 powders were produced by ball-milling Li_2CO_3 and TiO_2 in a 1:1 M ratio; they were then dried and calcined at 850 °C. LBSCA glass was prepared using a quenching method. The oxide raw materials were mixed and melted at 1000 °C for 2 h using an alumina crucible at a Li_2O:B_2O_3:SiO_2:CaO:Al_2O_3 molar ratio of 52.45:31.06:11.99:2.25:2.25 [16]. The solution was then quickly removed from the furnace and poured with cold water to obtain the glass. Afterwards, 0.25 wt% to 2 wt% of LBSCA was added into 0.86$CaWO_4$–0.14Li_2TiO_3 (0.86:0.14 was the weight ratio of the $CaWO_4$ and Li_2TiO_3 powders, which was calculated by their respective τ_f to obtain near-zero τ_f in the compound materials) mixtures before ball milling. After drying and mixing with an appropriate amount of acryloid polymer binder, the screened powders were pressed into cylinders by uniaxially pressing. These specimens were heated to 500 °C, maintained at this temperature for 4 h to remove the organic binder and then sintered at 850 °C to 950 °C for 3 h.

The Archimedes method was used to measure the bulk densities of the specimens. The relative densities were obtained by the ratios of the bulk and theoretical densities. The phase formation was analysed using X-ray diffraction (XRD: DX-2700) using Cu K_α radiation, and the micrographs of the specimens were analysed using scanning electron microscopy (SEM: JOEL JSM6490LV). The dielectric behaviours in microwave frequency were measured using the Hakki–Coleman method and Agilent N5230A network analyzer in a resonant cavity. The τ_f values were calculated as follows in a temperature range of 20 °C to 80 °C:

$$\tau_f = \frac{f_T - f_0}{f_0(T - T_0)} \tag{1}$$

where f_T and f_0 are the resonant frequencies at T and T_0, respectively.

3. Results and discussion

Fig. 1 shows the XRD patterns of the 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics with different LBSCA additions and sintered at 900 °C. All peaks were indexed in terms of $CaWO_4$ (♦, PDF #41-1431) and Li_2TiO_3(•, #33-0831). The Li_2TiO_3 phase favourably coexisted with

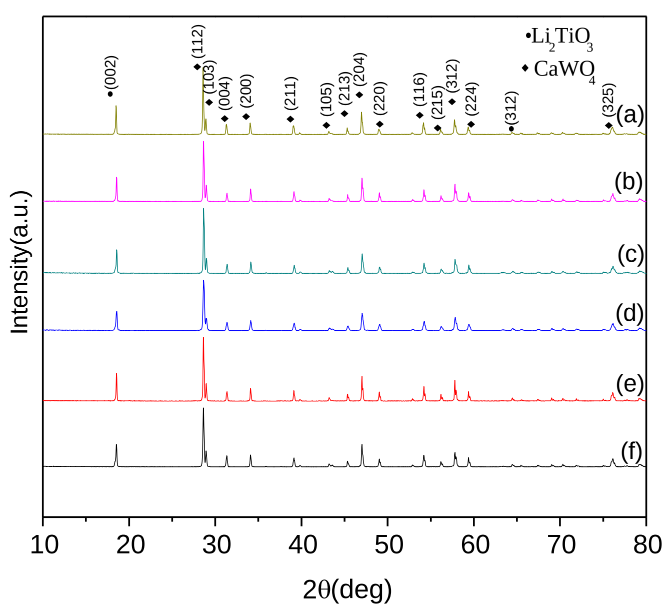

Fig. 1. XRD patterns of $CaWO_4$–Li_2TiO_3 ceramics with x wt% LBSCA additive and sintered at 900 °C for 3 h. (a) x=0, (b) x=0.25, (c) x=0.5, (d) x=0.75, (e) x=1 and (f) x=2.

the $CaWO_4$ phase in the 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics even though $CaWO_4$ belonged to the tetragonal scheelite system (space group $I4_{1/a}$ (No. 88)) [17], and Li_2TiO_3 belonged to the monoclinic crystal structure (space group $C_{2/c}$) [18]. No other new phase was produced during the sintering. LBSCA addition was undetectable, which suggested that LBSCA existed in an amorphous phase [19].

Fig. 2 presents the SEM micrographs of the 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics that are added with different LBSCA. LBSCA addition strongly affected the densification and average grain size of the compound ceramics. The pure 0.86$CaWO_4$–0.14Li_2TiO_3 ceramic in Fig. 2(a) exhibited a porous microstructure with many intergranular pores. Fig. 2(b) shows that the intergranular pores obviously decreased and that the grain size increased. Fig. 2 (c) shows the formation of a dense microstructure with few intergranular pores when the amount of LBSCA reached 0.5 wt%. However, Figs. 2(d)–(f) show that the microstructure did not demonstrate any obvious changes when the LBSCA content further increased. Therefore, a 0.5 wt% LBSCA addition was enough to obtain a dense microstructure with a homogeneous grain size.

Fig. 3 presents the relative densities of the 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics with the addition of different amounts of LBSCA. The relative densities obviously increased and reached their peak with 0.5 wt% LBSCA and then slightly decreased with a further increase in LBSCA content. An undoped specimen sintered at 900 °C showed a relative density of 86.5%, which increased to 94.8% after the addition of 0.5 wt% LBSCA. This outcome indicates that the liquid phase of LBSCA during sintering can effectively promote densification and reduce the sintering temperature of 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics. This phenomenon was also consistent with the variations in microstructure. The slight decrease in relative density with further increasing LBSCA glass content could be attributed to two reasons. One was the fact that excessive grain boundary amorphous LBSCA glass may hinder the further densification of the materials. The other reason was that the content ratio of low-density glass addition should contribute the decrease of densities of samples. Furthermore, with further increasing sintering temperature from 900 °C to 925 °C or 950 °C, density values presented a slight decrease on the contrary. This fact might be attributed to that higher sintering temperatures led to the decomposition of Li_2TiO_3 and appearance of closed pores. Therefore, the sample with 0.5 wt% LBSCA addition and sintered at 900 °C could obtain the highest relative density in these compound materials.

Fig. 4 shows the dielectric constant (ε_r) values of the 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics with different amounts of LBSCA and sintered at various temperatures. As expected, permittivity closely followed the variations of relative density in all cases, which indicated that ε_r was mainly determined by the density of the specimens. The specimen with $x=0$ achieved the lowest ε_r and relative density. As the LBSCA addition increased, ε_r gradually increased and reached its peak with 0.5 wt% LBSCA. However, ε_r slightly decreased with further LBSCA addition. Similar to the variation of density, this trend remained the same under different sintering temperatures.

Fig. 5 shows the *Qf* values of LBSCA-doped 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics as a function of sintering temperature ranging from 850 °C to 950 °C. The *Qf* values initially increased and then decreased with increasing LBSCA content. The specimen with 0.5 wt% LBSCA and sintered at 900 °C achieved the maximum *Qf* value of 76,000 GHz. Microwave dielectric loss may be divided into intrinsic and extrinsic losses [20]; intrinsic losses are dependent on the crystal structure and are mainly caused by lattice vibration modes, whereas extrinsic losses are associated with many factors, such as second phases, oxygen vacancies, grain sizes and densification or porosity [21]. Therefore, the initial increase of *Qf* values may be attributed to the increasing densification and average grain

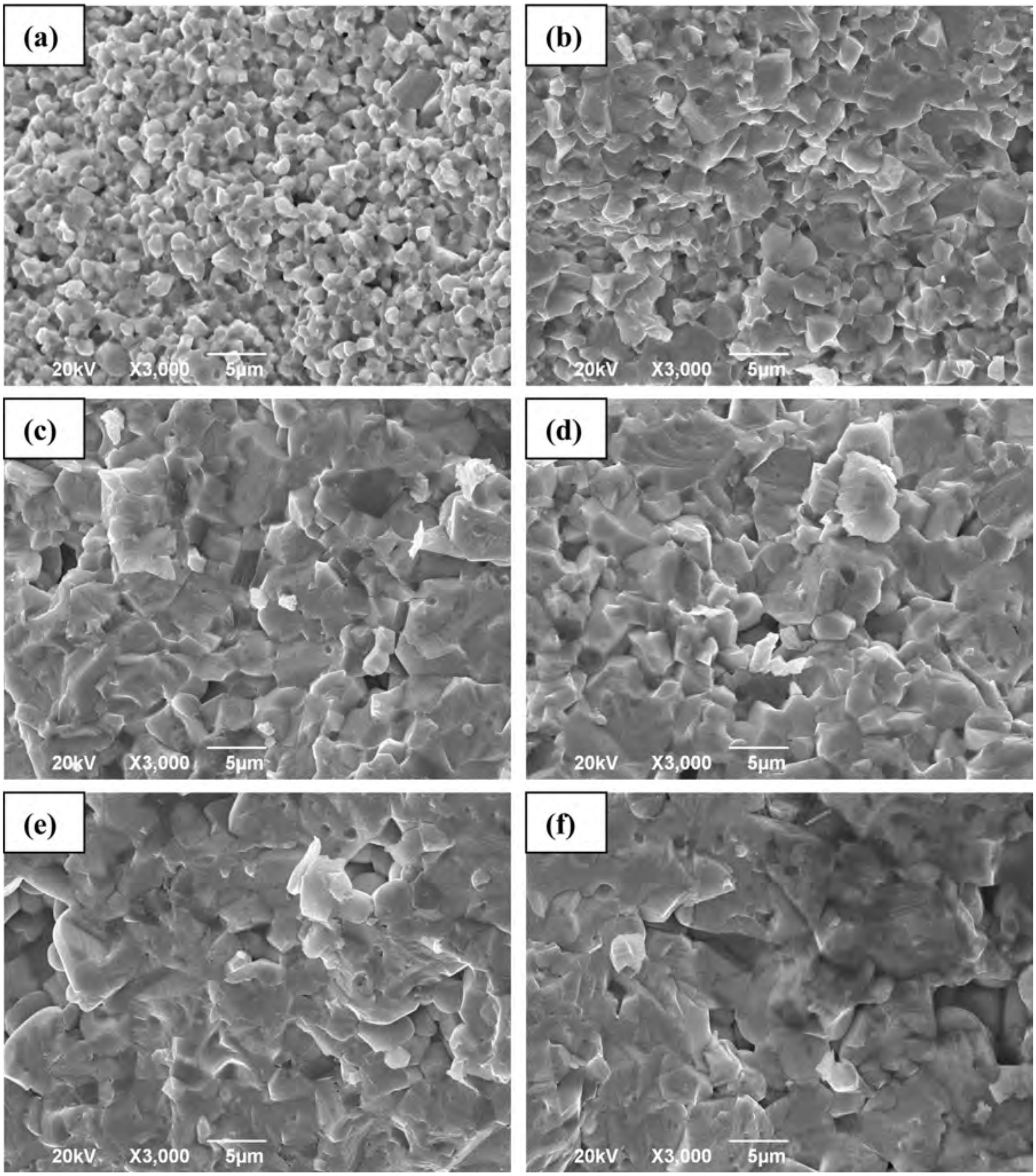

Fig. 2. SEM micrographs of $CaWO_4$–Li_2TiO_3 ceramics with x wt% LBSCA additive and sintered at 900 °C for 3 h. (a) x=0, (b) x=0.25, (c) x=0.5, (d) x=0.75, (e) x=1 and (f) x=2.

size, whereas the subsequent decrease of *Qf* values may be attributed to the reduced density and the excessively high loss of the liquid glass phase.

Fig. 6 shows the τ_f values of 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics sintered at 900 °C for 3 h in air. τ_f can be tuned by the formation of a solid solution or mixtures of dielectrics with opposite τ_f values [22]. The previous report showed that $CaWO_4$ had a τ_f value of −25 ppm/°C, whereas Li_2TiO_3 had a τ_f value of 35.05 ppm/°C. Therefore, near-zero τ_f values could be obtained through the compensation of the positive τ_f of Li_2TiO_3 and the negative τ_f of $CaWO_4$ in 0.86$CaWO_4$–0.14Li_2TiO_3. τ_f also slightly increased with increasing LBSCA glass content. The specimen with 0.5 wt% LBSCA and the highest *Qf* value obtained a τ_f of −2.9 ppm/°C, which was considered suitable for LTCC applications.

4. Conclusions

The effects of LBSCA addition on the phase formation, sintering character, microstructure and microwave dielectric properties of the 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics were investigated. The ceramics could be densified, and high *Qf* values could be obtained even with a small LBSCA addition. Near-zero τ_f values were obtained through the compensation of the positive τ_f of Li_2TiO_3 and the negative τ_f of $CaWO_4$. Typically, the 0.5 wt% LBSCA-doped 0.86$CaWO_4$–0.14Li_2TiO_3 ceramics sintered at 900 °C presented excellent microwave dielectric properties of ε_r=12.43, *Qf*=76,000 GHz and τ_f=−2.9 ppm/°C, thereby making these ceramics promising candidates for LTCC applications.

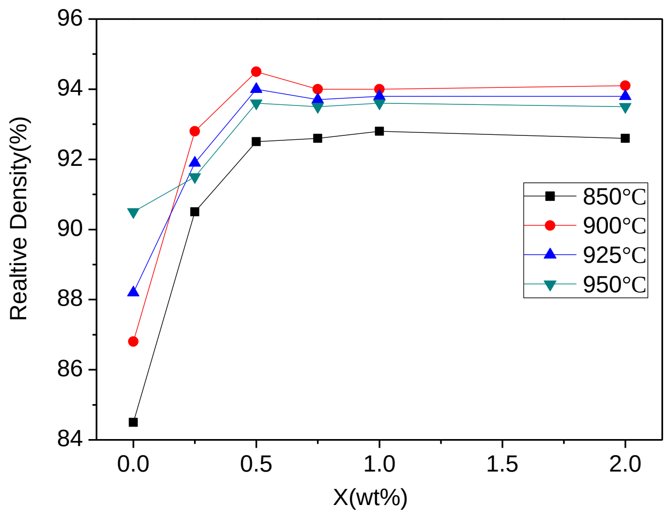

Fig. 3. Relative density of $CaWO_4$–Li_2TiO_3 ceramics with different LBSCA glasses and sintered at 850 °C to 950 °C.

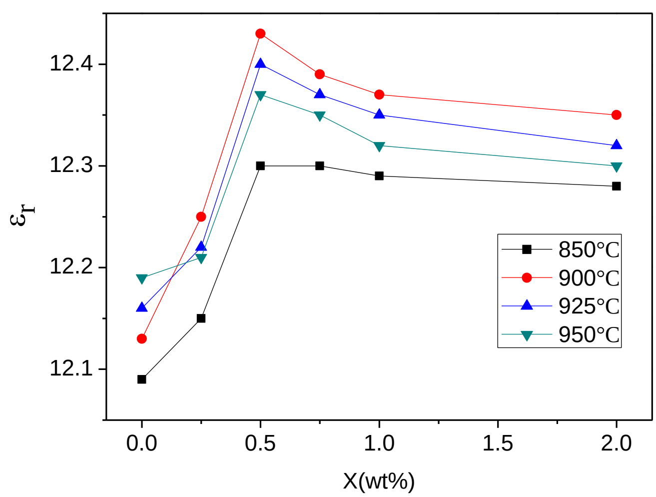

Fig. 4. Permittivity of $CaWO_4$–Li_2TiO_3 ceramics with different values of LBSCA glass content and sintered at 850 °C to 950 °C.

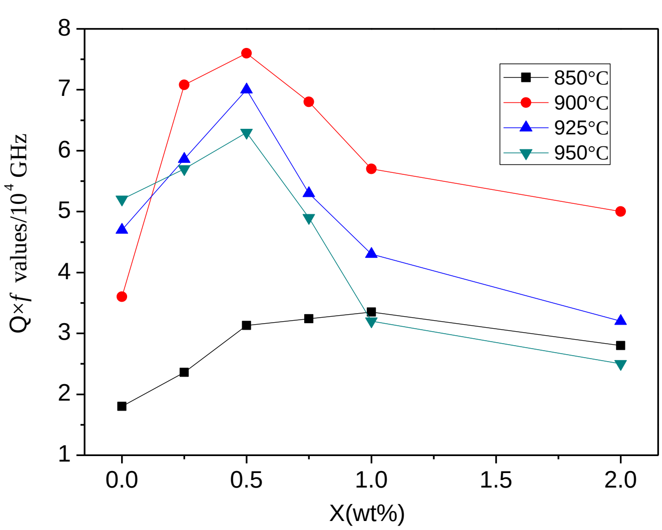

Fig. 5. *Qf* values of $CaWO_4$–Li_2TiO_3 ceramics with different LBSCA glass contents and sintered at 850 °C to 950 °C.

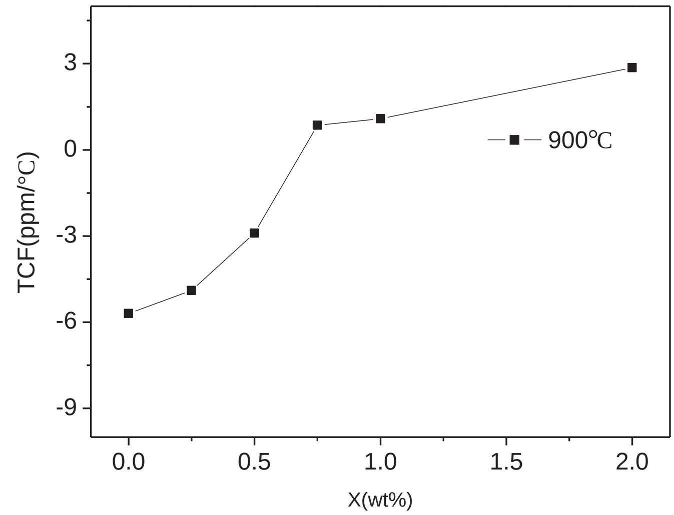

Fig. 6. τ_f values of $CaWO_4$–Li_2TiO_3 ceramics with x wt% LBSCA and sintered at 900 °C.

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