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High-Q microwave dielectric properties of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics for LTCC applications

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ABSTRACT

This study investigated the effects of Li_2O-MgO-ZnO_2-B_2O_3-SiO_2 (LMZBS) glass on the microstructure, sintering behaviour and microwave dielectric properties of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics. $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ powders were synthesised by a traditional solid-state route and added with different amounts of LMZBS glass (0–4 wt%) to decrease the sintering temperature of the ceramics to approximately 900 °C. The XRD patterns showed that no chemical reactions occurred between the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics and the LMZBS glass within the doping range. The SEM images indicated that the sample added with 1.5 wt% glass and sintered at 900 °C exhibited a compact and uniform microstructure. In particular, the microwave dielectric properties of the products were related to LMZBS glass content and sintering temperature. The sample with 1.5 wt% LMZBS glass exhibited excellent microwave dielectric properties, namely, ε_r=6.12, $Q\times f$=83,600 GHz and τ_f=−39.1ppm/°C.

1. Introduction

Various microwave materials and devices have been widely used and investigated for rapidly progressing microwave telecommunication industry, particularly in satellite communications and global positioning systems. Low-temperature co-fired ceramics (LTCC) technology are required to miniaturize and integrate microwave components for wireless communication [1,2]. LTCC materials should possess low permittivity (ε_r), high quality factor ($Q\times f$) and good dielectric thermal stability to be applicable for microwave communication [3–5]. Moreover, the sintering temperature of these ceramics should be lower than 900 °C so they could be co-fired with silver (Ag) electrode [6,7]. In general, LTCC materials can be fabricated using several methods, such as wet-chemistry route, use of ultrafine particles as raw materials and adding low melting temperature oxides or glass. Adding low melting temperature oxides or glass for liquid-phase sintering is the most effective and inexpensive method for decreasing the sintering temperature of LTCC ceramics.

Zn_2SiO_4 is a low-permittivity ceramic that has been widely investigated. Guo reported that Zn_2SiO_4 ceramics synthesised by traditional solid-state reaction exhibited excellent dielectric properties (ε_r=6.6, $Q\times f$=219,000 GHz and τ_f=−61ppm/°C) when sintered at 1340 °C [8]. However, the high sintering temperature of Zn_2SiO_4 limits its application in LTCC technology. Kim decreased the sintering temperature of $Zn_{2-x}SiO_{4-X}(0 < x < 0.5)$ ceramics from 1340 °C to 900 °C by adding 25 wt% B_2O_3 [9]. The $Q\times f$ values of the sample with x=0.3 reached the maximum value at 70,000 GHz. However, adding high amounts of B_2O_3 complicated the formation of casting film. Zhou reported that $(Zn_{0.95}Co_{0.05})_2SiO_4$ mixed with 1.5 wt% Li_2O–B_2O_3–Bi_2O_3–SiO_2 glass and sintered at 900 °C showed ε_r=6.16 and relatively high dielectric loss ($Q\times f$=33,000 GHz) [10]. To decrease both dielectric loss and sintering temperature, scholars must develop new methods with low amounts of sintering aid to produce materials with excellent microwave dielectric properties. Previous studies reported that lithium-substituted Li_2CaSiO_4, $LiAlSiO_4$ and Li_2ZnSiO_4 ceramics exhibited relatively low sintering temperature, low permittivity (< 10) and high quality factor [11–13]. A suitable strategy comprises two parts: first, moderate lithium-substituted ceramics are selected as substrate to decrease the sintering temperature without deteriorating the dielectric properties of the materials; second, low amounts of sintering aids are added to decrease the sintering temperature of the material systems to approximately 900 °C.

In this paper, a lithium ion-substituted $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramic sample was selected as substrate to obtain a product with relatively low dielectric loss, permittivity and sintering temperature. Different amounts of LMZBS glass (0–4 wt%) were used as sintering

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aid to decrease the sintering temperature of the ceramic systems. The effects of LMZBS glass on the sintering behaviour, microstructure and microwave dielectric properties of the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics were systematically investigated.

2. Experimental procedure

Ceramic samples were prepared by conventional solid-state reaction. Previous reported that cobalt ions that substituted zinc ions in the lattice sites of ZnO existed as Co^{2+} ions when Co_2O_3 was used as raw powder [14,15]. In the present study, high-purity oxides such as Li_2CO_3(99%), ZnO(99%), SiO_2(99%) and Co_2O_3(99%) were used as raw materials and weighed according to the stoichiometric formula $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$. The oxides were ball milled with ZrO_2 balls and deionised water in a nylon jar for 6 h. The resultant slurry was dried and calcined at 850–1150 °C in air for 4 h. The powder samples were added with 2 wt% LMZBS glass and calcined at different temperatures to determine the optimal calcination temperature of the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramic. The mixtures were then remilled for 12 h. The powders were dried, ground with polyvinyl alcohol solution, granulated and pressed into cylindrical specimens. These specimens were finally sintered at 900 °C. The powders calcined at the optimal temperature were added with different amounts of LMZBS glass (0–4 wt%). The mixtures were remilled, dried, granulated and pressed into cylindrical specimens according to the processes described above. The specimens were sintered from 850 °C to 950 °C for 3 h. The LMZBS glass used in this study was prepared through quenching. Analytical-grade raw materials were weighed at a molar ratio of Li_2O:MgO:ZnO:B_2O_3:SiO_2=20:20:20:20:20. The mixed powders were ball milled, dried and melted in alumina crucible at 1350 °C for 3 h. The solution was rapidly removed from the furnace and quenched into cold distilled water to obtain the glass.

The crystalline phases and structural properties of the samples were identified by X-ray diffraction analysis (XRD:DX-2700) using Cu Kα radiation. Microstructure was evaluated using scanning electron microscopy analysis (SEM: INCA penta FETX3 oxford). The bulk densities of the sintered samples were measured using Archimedes method. The microwave dielectric properties of the sintered ceramics were assessed by Hakki–Coleman resonator method and Agilent N5230A network analyser (300 MHz–20 GHz) in a resonant cavity. The temperature coefficient of resonant frequency (τ_f) was estimated by open cavity method using the following formula for the temperature range of 20–80 °C:

$$\tau_f = \frac{f_T - f_0}{f_0 (T - T_0)} \times 10^6 \quad (1)$$

where $f_T$and f_0 are the resonant frequencies at 80 °C and 20 °C, respectively; and T and T_0 are 80 °C and 20 °C, respectively.

3. Results and discussion

Fig. 1 shows the influence of calcination temperature on the sintering density and dielectric properties of the fabricated $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics. The $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ powder added with 2 wt% LMZBS glass was calcined at 850–1150 °C for 4 h and sintered at 900 °C for 3 h. The bulk density and permittivity of the ceramics increased gradually with increasing calcination temperature up to 1050 °C and then decreased thereafter. Similarly, the $Q\times f$ values peaked (around 69,500 GHz) when the sample was calcined at 1050 °C. Lithium is volatile and evaporates at high temperatures [16]. The first increase in the density, permittivity and $Q\times f$ value could be due to the function of the lithium ions in promoting the sintering process and improving the degree of densification. The subsequent decrease in the bulk density and dielectric properties of the sample calcined at temperatures higher than 1050 °C might be attributed to lithium

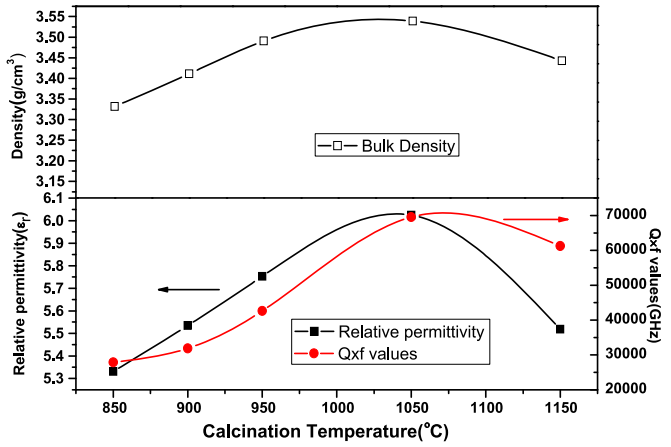

Fig. 1. Variations in bulk density and dielectric properties with increasing calcination temperature of the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics.

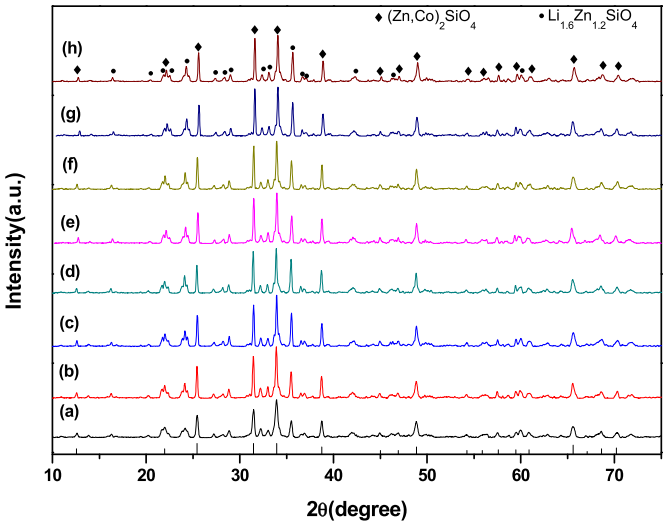

Fig. 2. XRD diffraction patterns of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics with x wt% LMZBS calcined at 1050 °C/4 h and sintered at 900 °C for 3 h. (a) x=0, (b) x=0.5, (c) x=1, (d) x=1.5, (e) x=2, (f) x=2.5, (g) x=3, and (h) x=4.

volatilisation. In general, 1050 °C was considered the optimal calcination temperature to obtain $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics with high performance.

Fig. 2 shows the XRD diffraction patterns of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics added with x wt% LMZBS and sintered at 900 °C for 3 h. The stick pattern of $(Zn,Co)_2SiO_4$ was plotted at the bottom of Fig. 2. All samples contained only two phases: the main phase $(Zn,Co)_2SiO_4$ (◆, PDF #46–1316) and the minor phase $Li_{1.6}Zn_{1.2}SiO_4$ (•, PDF #24–0676). All diffraction patterns of the samples were almost unanimous, indicating that the presence of LMZBS did not promote the production of a new phase. Furthermore, the added LMZBS was undetected, suggesting that LMZBS existed in the amorphous phase.

The SEM images of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics added with x wt% LMZBS and sintered at 900 °C are shown in Fig. 3. The samples presented a porous microstructure with small average grain size [Fig. 3(a) and (b) 0 and 0.5 wt% LMZBS glass]. As the LMZBS glass content increased, the samples became denser, and the average grain size increased. Particularly, the sample with 1.5 wt% LMZBS glass possessed a compact and uniform microstructure. The presence of LMZBS glass decreased the porosity and improved the growth of grains via the liquid-phase sintering effect. However, further increasing the LMZBS glass content led to the formation of deteriorative microstructures with inconsistent grain shape and abnormal grain growth [Fig. 3(e)-(g)] and evident pores [Fig. 3(h)].

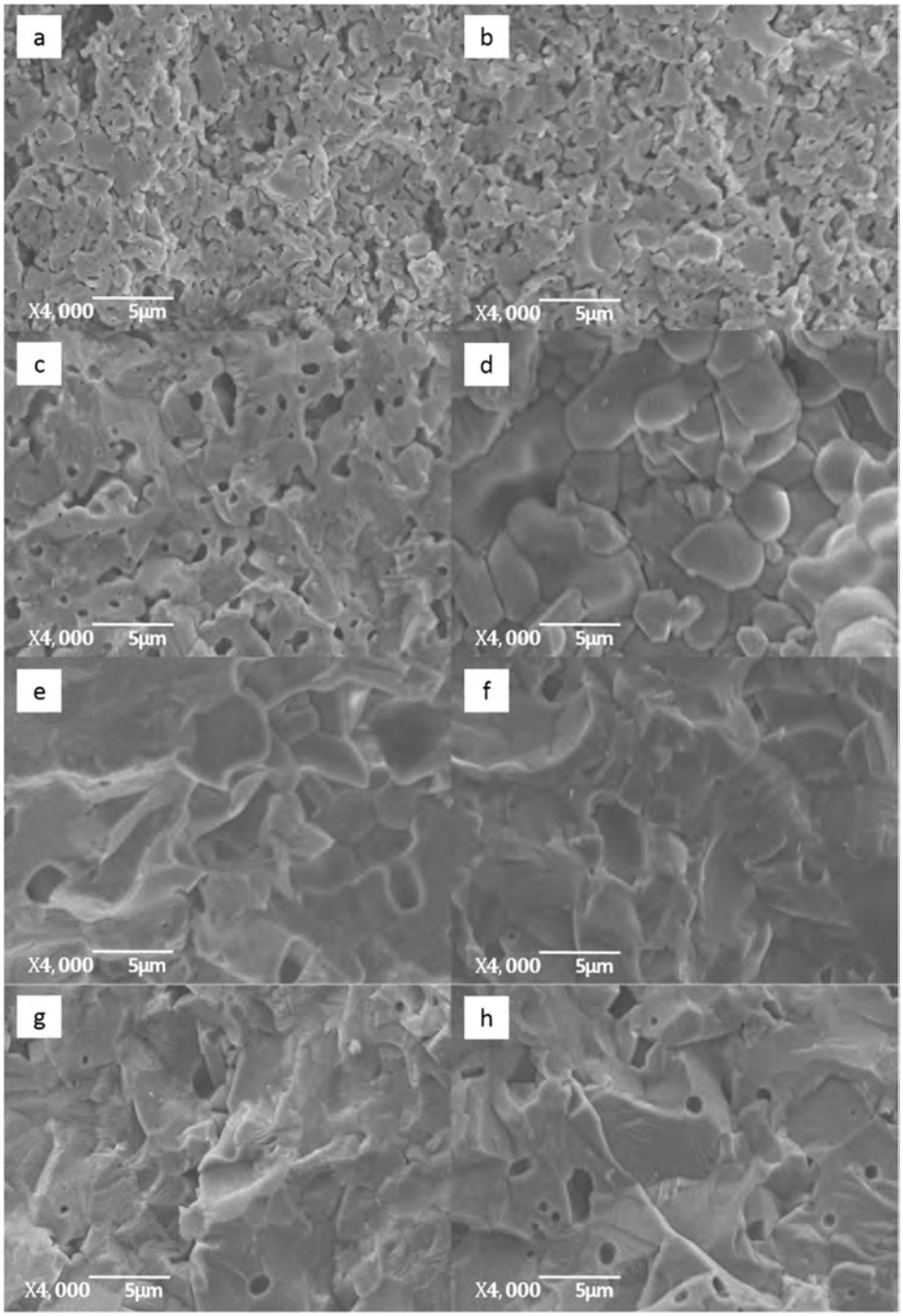

Fig. 3. SEM micrographs of the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics with x wt% LMZBS and sintered at 900 °C for 3 h. (a)x=0, (b)x=0.5,(c)x=1,(d)x=1.5,(e)x=2, (f)x=2.5,(g)x=3,(h)=4.

Fig. 4 illustrates the influence of LMZBS content on the bulk density and ε_r of the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics sintered at 850–950 °C. The bulk densities were calculated by the formula (Archimedes method):

$$\rho = \frac{m_1}{m_2} \times \rho_w \tag{2}$$

where ρ and ρ_w are the densities of the specimen and distilled water; and m_1 and m_2 are the masses of the specimen in air and distilled water, respectively. The bulk densities of the samples increased with increasing LMZBS up to 1.5 wt% (sintered at 900 °C and 950 °C) and 2.5 wt% (sintered at 850 °C). When the amount of LMZBS was further increased, the bulk densities of the samples gradually decreased. In general, adding appropriate amount of glass could improve densification because the glassy liquid phase at the grain boundary eliminated the porosity and thus increased the bulk density of the material. However, adding high amounts of glass could decrease the sintering density possibly because of three reasons. First, excessive amorphous LMZBS glass at the grain boundary might hinder the densification of the ceramics [17]. Second, trapped porosity, which is associated with grain growth and formation of pores by evaporation of excess glass components, may decrease the bulk densities for high glass fluxing [18]; this phenomenon is consistent with the SEM images in Fig. 3. Third, the density of the LMZBS glass (2.35 g/cm^3 [19]) is lower than that of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramic, resulting in decreased density of the material systems. Similarly, the variation in ε_r in samples added

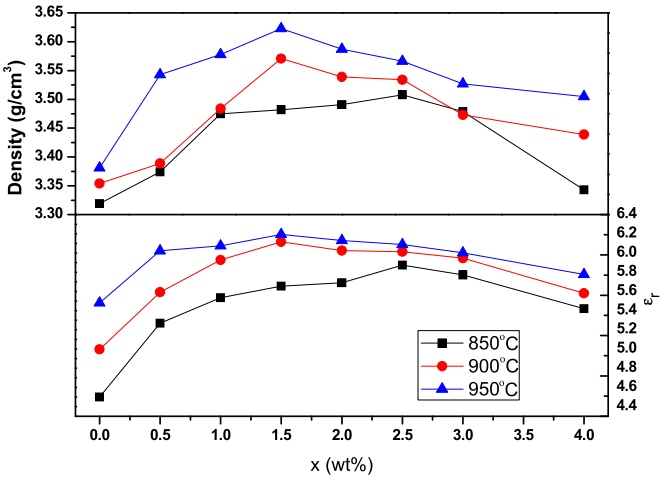

Fig. 4. Variation in the bulk density and permittivity of the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics sintered at 850–950 °C for 3 h with x wt% LMZBS.

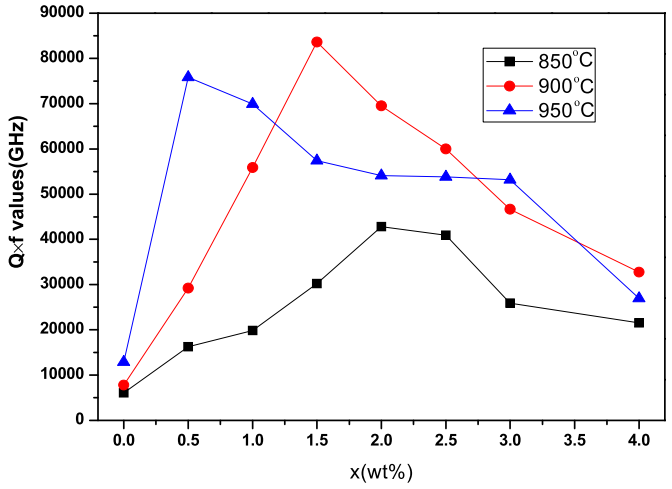

Fig. 5. $Q\times f$ values of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics with x wt% LMZBS and sintered at 850–950 °C for 3 h.

with different amounts of LMZBS and sintered at 850–950 °C presented a trend of increasing first and then decreasing [20]. Hence, ε_r was considerably influenced by sintering density. Overall, adding a small amount of glass increased the relative permittivity to the maximum, whereas excessive addition of glass decreased the permittivity of the material systems [21]. For example, the relative permittivity of the sample sintered at 900 °C increased from 4.99 to 6.12 when added with 1.5 wt% LMZBS glass and then decreased to 5.58 when added with 4 wt% LMZBS. The enhanced densification also increased the relative permittivity, and reduction in densification could decrease the relative permittivity. Furthermore, the increase in the low-dielectric glass content decreased the dielectric constant.

Fig. 5 presents the variations in $Q\times f$ values depending on LMZBS content and sintering temperature of the $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics. The $Q\times f$ values initially increased and then decreased with increasing LMZBS content. At the point of x=0, the $Q\times f$ values of the samples sintered at 850–950 °C were low. The $Q\times f$ values increased significantly with increasing amount of LMZBS glass added. Particularly, the sample added with 0.5 wt% LMZBS glass and sintered at 950 °C reached the maximum $Q\times f$ value (around 75,800 GHz). Analogously, the specimens sintered at 850 °C and 900 °C (around 42,800 and 836,00 GHz) reached their peak values at x=2 and x=1.5, respectively. The $Q\times f$ values decreased gradually when sintered at 850–950 °C and with further increase in the LMZBS content. The $Q\times f$ values exhibited a similar tendency to the bulk densities of the

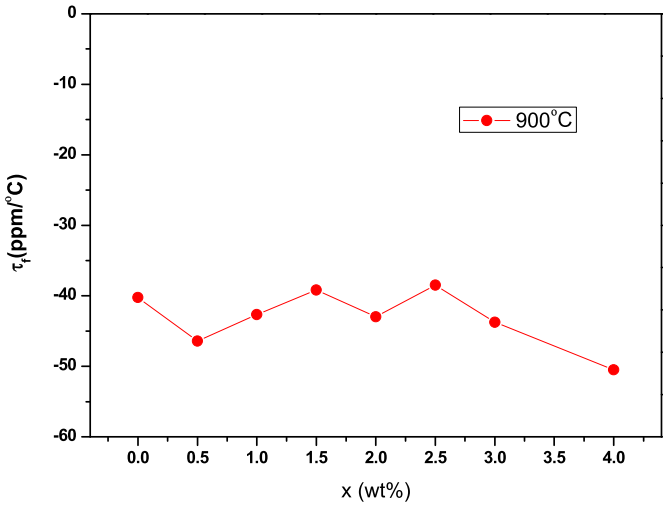

Fig. 6. τ_f values of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics with x wt% LMZBS glass and sintered at 900 °C for 3 h.

$Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics (Fig. 4). Thus, the quality of the fabricated $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics was significantly relevant to densification. Furthermore, microstructures with dense and uniform grain size contributed to the high $Q\times f$ values of the specimen added with 1.5 wt% LMZBS [Fig. 3(d)]. However, a slight difference was observed between Figs. 4 and 5. The samples sintered at 950 °C showed higher bulk densities but lower $Q\times f$ values than those of the products sintered at 900 °C. Generally, microwave dielectric loss comprises intrinsic and extrinsic losses, with the latter playing a more important role [10]. The grains would grow abnormally when the sample was sintered at or higher than the optimal temperature [22]. In the present study, abnormal grain growth occurred when the sample was sintered at 950 °C, leading to reduced $Q\times f$ values. As shown in Fig. 3(e)–(h), adding excessive LMZBS content could also decreased the $Q\times f$ values. Excessive liquid–glass phase could also reduce the $Q\times f$ values [12].

Fig. 6 shows the τ_f(TCF) values of $Li(Zn_{0.95}Co_{0.05})_{1.5}SiO_4$ ceramics added with x wt% LMZBS glass and sintered at 900 °C for 3 h in air. The τ_f values showed insignificant variation, ranging from −38.5 ppm/°C to −50.5 ppm/°C. The sample with τ_f value of −39.1 ppm/°C showed the optimal dielectric properties.

4. Conclusion

In this study, adding low amounts of LMZBS glass combined with a lithium ion-substitution effectively reduced the sintering temperature of the $(Zn_{0.95}Co_{0.05})_2SiO_4$ ceramics from 1300 °C to 900 °C. The XRD patterns indicated that LMZBS glass (lower than 4 wt%) did not promote the formation of a new phase. The sample added with 1.5 wt% LMZBS and sintered at 900 °C possessed compact microstructure with uniform grain size. The sample also exhibited excellent dielectric properties of ε_r=6.12, $Q\times f$=83,600 GHz and τ_f=−39.1ppm/°C.

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