Effects of LiF on sintering characteristics and dielectric properties of low-loss SrCuSi$_4$O$_{10}$ ceramics for LTCC applications

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HIGHLIGHTS

- The sintering temperature of SrCuSi$_4$O$_{10}$ ceramics reduced to 900 °C from 1100 °C.
- The main peak exhibited a slight shift toward the higher 2θ degrees.
- The τ_ε can be effectively modified to near zero by changing the TiO$_2$ content.
- SrCuSi$_4$O$_{10}$-1.0 wt% LiF-21 wt% TiO$_2$ ceramics exhibited good dielectric properties.

ARTICLE INFO

ABSTRACT

The SrCuSi$_4$O$_{10}$-*x* wt% LiF (*x* = 0.5, 1.0, 1.5, 2.0) ceramics were prepared by the conventional solid-state route. The effects of LiF on the sintering behavior, microstructure, phase evolution and dielectric properties of the SrCuSi$_4$O$_{10}$ ceramics were systematically investigated. And the sintering temperature of SrCuSi$_4$O$_{10}$ ceramics has been reduced to 900 °C from 1100 °C with a certain amount of LiF. The SrCuSi$_4$O$_{10}$ ceramics with 1.0 wt% LiF addition sintered at 900 °C for 6 h exhibited excellent dielectric properties of $\varepsilon_r \sim 5.88$, $\tan\delta \sim 1.6 \times 10^{-3}$, $\tau_\varepsilon \sim 119.90$ ppm/°C. However, the relatively large positive τ_ε was unfavorable to practical applications. Hence, the TiO$_2$ that owned a considerable negative τ_ε was introduced to obtain a desired τ_ε value. The addition of 21 wt% TiO$_2$ effectively improved the temperature stability of ceramics and τ_ε was adjusted to near zero. The prepared SrCuSi$_4$O$_{10}$-1.0 wt% LiF-21 wt% TiO$_2$ ceramics sintered at 900 °C for 6 h showed fairly good dielectric properties of $\varepsilon_r \sim 6.73$, $\tan\delta \sim 3.7 \times 10^{-3}$, $\tau_\varepsilon \sim 1.80$ ppm/°C.

1. Introduction

With the development of wireless communication systems, microwave dielectric materials have attracted great interests for advantages on passive components, such as resonators, antennas and filters [1]. In order to satisfy the demands for miniaturization, packaging and integration of various microwave devices, the low temperature co-fired ceramic (LTCC) technology has attracted considerable attentions owing to the ability to combine the multi-layer ceramics and conductors for various modules and substrates [2–5]. For practical applications, the LTCC substrate materials should possess low dielectric loss (tanδ), low dielectric constant (ε_r) to reduce signal delay, and near-zero temperature coefficient of dielectric constant (τ_ε) for stability [6–8]. Silicates, a candidate of substrate materials, own low ε_r due to the silica-oxygen tetrahedra composed of half covalent bonds [9,10]. Wesselsite (SrCuSi$_4$O$_{10}$), which was first systematically reported by Manu et al.,

showed a low $\varepsilon_r \sim 5.05$ and $\tan\delta \sim 9.6 \times 10^{-4}$ at 1 MHz when sintered at 1100 °C for 6 h [11]. However, the required high sintering temperature of SrCuSi$_4$O$_{10}$ ceramics restricted the practical applications in the LTCC field. The sintering temperature of LTCCs should be lower than the melting point of the common electrode materials, such as Ag (961 °C) and Cu (1083 °C) [12,13]. Therefore, it is significant to lower the sintering temperature of ceramics to meet the requirements of LTCC applications.

Recently, in order to lower the sintering temperature of ceramics, many strategies have been proposed. The approach of adding low melting point materials to ceramics is widely used to lower the densification temperature of dielectric ceramics [14–16]. It is well known that lithium fluorite (LiF) is an effective sintering aid for various materials. Li$^+$ is an easily diffused ion at low temperature, which makes it be a very efficient sintering additive for many materials [17–20]. What's more, in order to attain the temperature compensation of

dielectric constant, the materials with opposite τ_ε are used to obtain a desired τ_ε value. In our previous study, the τ_ε of $SrCuSi_4O_{10}$ ceramics is a relatively large and positive value [21]. Therefore, we should introduce some material that owns a big and negative τ_ε value, such as TiO_2, to tune the τ_ε to near zero.

In this work, LiF was used as sintering aid and TiO_2 was employed as τ_ε compensator. We toke two steps to obtain the low-temperature co-fired ceramics with excellent dielectric properties. Firstly, a small amount of LiF was considered to lower the densification temperature of $SrCuSi_4O_{10}$ ceramics. Then, the $SrCuSi_4O_{10}$-LiF ceramics were mixed with TiO_2 to tune the τ_ε. The effects of LiF on the sintering characteristics, microstructures and dielectric properties of $SrCuSi_4O_{10}$ ceramics with addition of TiO_2 were investigated systematically.

2. Experimental procedure

The $SrCuSi_4O_{10}$ ceramics were synthesized by the conventional solid-state reaction method using high purity powders of $SrCO_3$ (99.0%), CuO (99.0%) and SiO_2 (99.0%). The starting materials were ball-milled with distilled water for 6 h according to the stoichiometric compositions of $SrCuSi_4O_{10}$. The mixtures were dried, crushed and sieved with a 40 mesh screen. Then the sieved samples were calcined at 975 °C for 4 h in air. Afterwards, $SrCuSi_4O_{10}$-x wt% LiF (x = 0.5, 1.0, 1.5, 2.0) and $SrCuSi_4O_{10}$-1.0 wt% LiF-y wt% TiO_2 (y = 15, 18, 21, 24) mixtures were prepared by pure $SrCuSi_4O_{10}$, LiF and TiO_2 powders and re-milled for 6 h. After dried, paraffin was added to the powders as a binder. Pellets of 15 mm in diameter and 6–7 mm in thickness were prepared under a pressure of 4 MPa by uniaxial pressing. Then, the obtained pellets were sintered at 800–950 °C for 6 h in air with the heating rate of 3 °C/min.

The bulk densities of the sintered ceramics were measured by the Archimedes method. The crystalline phases were identified by X-ray diffraction (XRD) (Rigaku D/max 2550 PC, Tokyo, Japan) with Cu Kα radiation (V = 200 kV, I = 40 mA) over a 2θ angle from 10° to 70°. The microstructures of the sintered samples were observed and analyzed by a scanning electron microscopy (SEM) (MERLIN Compact, Germany). The microwave dielectric properties of sintered samples were measured by a high precision LCR meter (Agilent E4981A, USA) at a frequency of 1 MHz on silver-plated pellets. The τ_ε was also measured by the LCR meter (Agilent E4981A, USA) at a frequency of 1 MHz with a thermostat in the temperature range from 25 °C to 85 °C and was calculated by the following formula:

$$\tau_\varepsilon = \frac{\varepsilon_{85} - \varepsilon_{25}}{\varepsilon_{25}(85 - 25)} \times 10^6 (ppm/°C)$$

Where ε_{25} and ε_{85} were the dielectric constants at 25 °C and 85 °C, respectively.

3. Results and discussion

3.1. $SrCuSi_4O_{10}$-LiF system

Fig. 1 showed the X-ray diffraction patterns of $SrCuSi_4O_{10}$ ceramics with 0.5, 1.0 and 1.5 wt% LiF sintered at 900 °C and 2.0 wt% LiF sintered at 875 °C for 6 h in air respectively. The peaks were indexed by the standard JCPDS file for $SrCuSi_4O_{10}$ (PDF #49-1813) and no additional peaks were observed. That indicated that there was no chemical reaction between $SrCuSi_4O_{10}$ and LiF. The main peak (202) shift was enlarged separately and plotted in Fig. 1. It was interesting to note that the main peak (202) exhibited a slight shift toward the higher 2θ degrees with increasing LiF addition when sintered at 900 °C shown in Fig. 1. As was well known, the shift of the peak position was associated with the variation of cell volume. Thus, the unit cell volume decreased due to the substitution of the F$^-$ ion in the O^{2-} sites considering their relative ionic sizes (radius F$^-$ = 1.33 Å, radius O^{2-} = 1.40 Å) [22]. When adding 2.0 wt% LiF to the samples sintered at 875 °C, the main
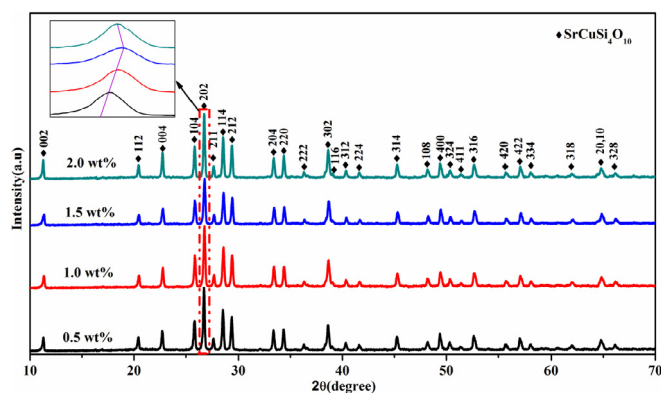

Fig. 1. The XRD patterns of the $SrCuSi_4O_{10}$ ceramics sintered at 900 °C for 6 h with (a) 0.5 wt%, (b)1.0 wt%, (c)1.5 wt% and sintered at 875 °C with (d) 2.0 wt % LiF.

peak (202) slightly shifted to a lower degree, one possible assumption was that the liquid phase during sintering process inhibited the entrance or occupation of F$^-$ in the $SrCuSi_4O_{10}$ lattice.

Typical SEM micrographs of the surfaces of $SrCuSi_4O_{10}$–x wt% LiF ceramics sintered at different temperatures were illustrated in Fig. 2. For the samples sintered at 900 °C, the pores decreased with the increasing x, as shown in Fig. 2 (a)–(c). When 0.5 wt% LiF was added, the ceramic samples sintered at 900 °C were highly porous, which indicated that the amount of the liquid phase was insufficient for sintering of the $SrCuSi_4O_{10}$ ceramics. In contrast to that, in the samples added with 1.0–1.5 wt% LiF sintered at low temperature, no obvious pores could be detected, which indicated the addition of LiF in improving the sintering behavior was effective. However, for the samples containing 2.0 wt% LiF, a higher porosity of sample surface was observed, which led to a decrease in microwave dielectric properties. Therefore, it was demonstrated that while a moderate amount of LiF improved the sinterability at low temperature, an excessive addition of sintering aid would remain in grain boundary.

Fig. 3 illustrated the bulk densities of $SrCuSi_4O_{10}$ ceramics with LiF addition as a function of sintering temperature. The concentration of the LiF strongly influenced the bulk density of the samples and the densification temperature was sharply lowered with the increasing LiF content. It could be observed that the bulk densities of $SrCuSi_4O_{10}$ ceramics increased with the increment of sintering temperature. And the density of the samples ascended to a maximum value of 3.06 g/cm^3,
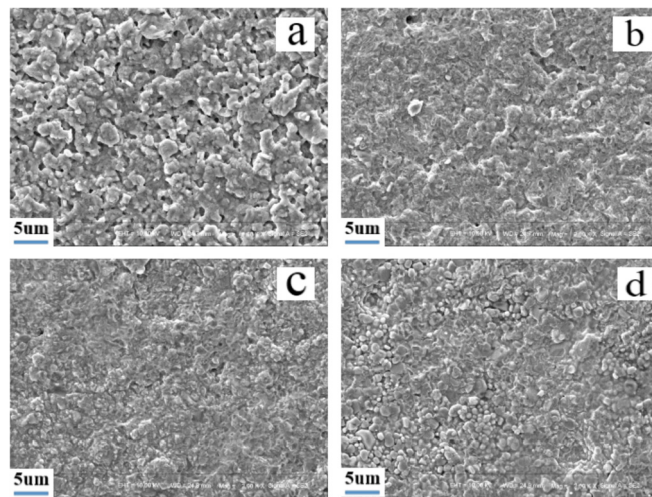

Fig. 2. The SEM micrographs of $SrCuSi_4O_{10}$-x wt% LiF ceramics sintered at 900 °C for 6 h: (a) x = 0.5 (b) x = 1.0 (c) x = 1.5, and sintered at 875 °C: (d) x = 2.0.
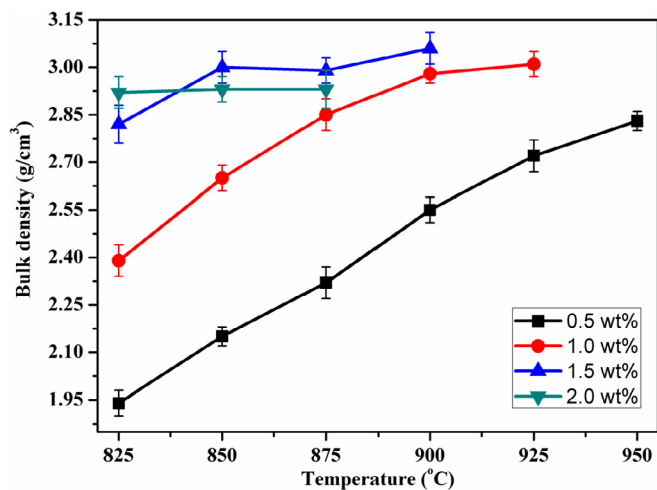
Fig. 3. The bulk density of SrCuSi$_4$O$_{10}$ ceramics with x wt% LiF as a function of sintering temperature.

Fig. 5. The tanδ values of SrCuSi$_4$O$_{10}$ ceramics with x wt% LiF as a function of sintering temperature.

when the SrCuSi$_4$O$_{10}$ ceramics with 1.5 wt% LiF addition were sintered at 900 °C. Moreover, the bulk density of the samples increased sharply with the sintering temperature when low level LiF (0.5 wt%) was added, which indicated that the 0.5 wt% LiF was not enough to improve the densification of SrCuSi$_4$O$_{10}$ ceramics effectively at the relatively low sintering temperatures. For the specimens with x = 2.0, with the increase of temperature, the changes of bulk density were not obvious. It was well known that a large extent of liquid phase was not favorable for mass transport and LiF had a relatively lower theoretical density of 2.635 g/cm^3 compared with the SrCuSi$_4$O$_{10}$ ceramics. Therefore, for the samples with higher content of LiF, the bulk density was not significantly improved. All the results demonstrated that the LiF additive was an effective sintering aid for SrCuSi$_4$O$_{10}$ ceramics.

Fig. 4 showed the dielectric constant of SrCuSi$_4$O$_{10}$ ceramics with different amount of LiF addition as a function of sintering temperature. Obviously, the relationship between ε_r value and sintering temperature showed the same trend as the relationship between bulk density and sintering temperature. It was known that the ε_r usually depended on the bulk density, second phase and porosity [23]. In this work, it was obvious that the ε_r values were mainly dependent on the bulk density and pores due to the obtained single phase as shown in Fig. 1. Thus, the SrCuSi$_4$O$_{10}$-0.5 wt% LiF ceramics with a low bulk density had a lower dielectric constant than others.

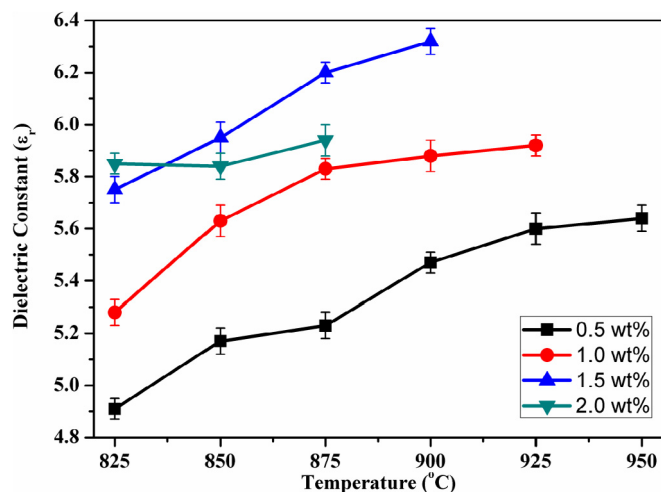The dielectric loss of the SrCuSi$_4$O$_{10}$ ceramics at 1 MHz with LiF
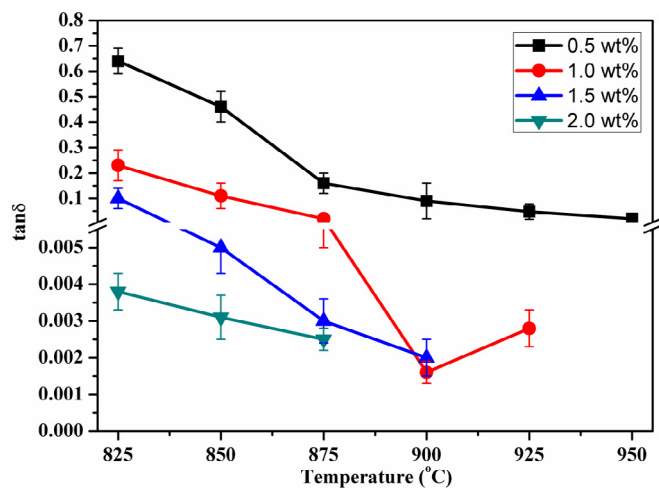
addition as a function of sintering temperature was shown in Fig. 5. It was well known that dielectric loss was mainly caused not only by the lattice vibration modes but also by porosity, second phase, lattice defect and grain boundary or grain morphology [23–26]. LiF-added samples, the variation of tanδ with sintering temperatures was similar to that of bulk density, suggested that the density was the dominating factor to control tanδ in SrCuSi$_4$O$_{10}$ ceramics. For slight amount of LiF-added samples (x = 0.5), it could be observed that the tanδ values decreased with the increasing sintering temperature. By contrast, the tanδ value of SrCuSi$_4$O$_{10}$ ceramics with 1.0 wt% LiF decreased with the increasing sintering temperature then increased after reaching their respective minimum value. The decrease in the tanδ value could be solely attributed to an increase in the density, whereas its increase at higher temperature was due to the excessive liquid phase by LiF addition at the grain boundaries. This illustrated that the amount of additives required less and less as the temperature increased in order to achieve the same density and excellent dielectric properties. And the results of SrCuSi$_4$O$_{10}$ ceramics with 1.5 and 2.0 wt% LiF also proved this. For SrCuSi$_4$O$_{10}$ ceramics with 1.5 wt% LiF, the samples melted in the container when the sintering temperature exceeded 900 °C. The maximum sintering temperature of SrCuSi$_4$O$_{10}$ ceramics with 2.0 wt% LiF was 875 °C. Typically, the optimum tanδ ∼ 1.6 × 10^{-3} at 1 MHz was obtained in SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramics sintered at 900 °C.

Fig. 6 indicated the temperature coefficients of dielectric constant values of SrCuSi$_4$O$_{10}$ ceramics sintered at 875 °C and 900 °C as a function of LiF content. The τ_ε values basically increased nonlinearly to more positive values as x increased and shifted from 121.08 to 132.96 ppm/°C with LiF content increasing from 0.5 to 2.0 wt% sintered at 875 °C. And the changes of τ_ε values were not obvious between different temperatures, which indicated that the τ_ε values were not sensitive to the sintering temperature. It was well known that the temperature coefficient predominantly depended on crystal structure and lattice parameter of the materials [27]. Therefore, it could be reasonably believed that the variation of τ_ε values should be closely related to the substitution of the F$^-$ ion in the O^{2-} site, which resulted in the unit cell volume decreased.

3.2. SrCuSi$_4$O$_{10}$-LiF-TiO$_2$ system

In order to adjust the τ_ε close to zero, TiO$_2$ was added into SrCuSi$_4$O$_{10}$-1.0 wt% LiF samples. Fig. 7 showed the XRD patterns of SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramic modified with 15–24 wt% TiO$_2$ sintered at 900 °C in air for 6 h. Besides the main phase SrCuSi$_4$O$_{10}$, an amount of TiO$_2$ phase were detected when TiO$_2$ was added. And the variation of the intensity of secondary phases was not obvious with

Fig. 4. The dielectric constant of SrCuSi$_4$O$_{10}$ ceramics with x wt% LiF as a function of sintering temperature.
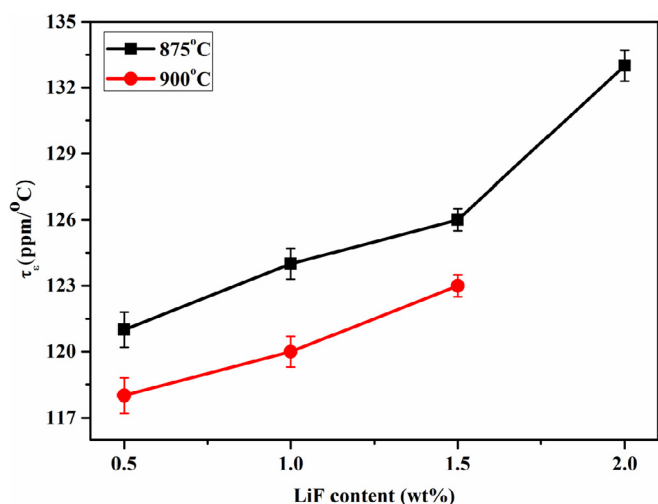
Fig. 6. The τ_ε values of SrCuSi$_4$O$_{10}$ ceramics with *x* wt% LiF sintered at 900 °C and 875 °C for 6 h.
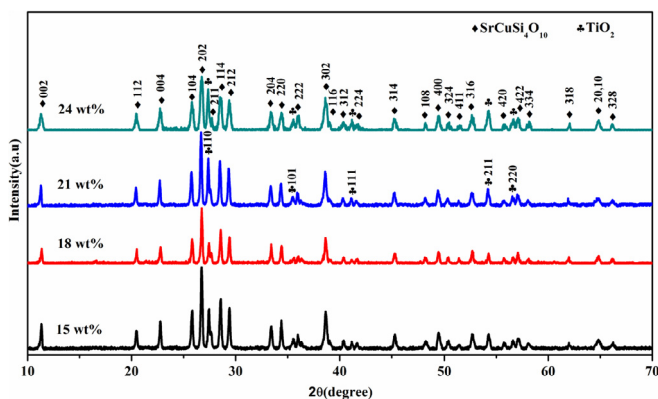

Fig. 7. The XRD patterns of the SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramics sintered at 900 °C for 6 h with (a) 15 wt%, (b) 18 wt%, (c) 21 wt% and (d) 24 wt% TiO$_2$.

Fig. 8. Bulk density, dielectric constant and tanδ of SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramics with *y* wt% TiO$_2$ sintered at 900 °C for 6 h.

Fig. 9. The τ_ε values of SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramics with *y* wt% TiO$_2$ sintered at 900 °C for 6 h.

increasing the TiO$_2$ content.

The bulk density, dielectric constant, and dielectric loss of SrCuSi$_4$O$_{10}$ ceramics as a function of the TiO$_2$ content were shown in Fig. 8. It could be observed that the bulk densities increased, as the TiO$_2$ content increased from 15 to 24 wt%. And the bulk density increased from 3.05 to 3.21 g/cm^3 with the changing of TiO$_2$ content because TiO$_2$ possessed a higher bulk density (4.236 g/cm^3). The ε_r value revealed rather similar tendency with the bulk density, since the higher bulk density meant lower porosity. Besides, it was well known that TiO$_2$ had a higher dielectric constant ($\varepsilon_r \sim 105$) [28]. Therefore, it could also explain why the ε_r value increased from 6.42 to 6.85. In addition, a sustained upward trend in the tanδ value increasing from 2.7×10^{-3} to 5.4×10^{-3} was observed, as the TiO$_2$ content increased.

Fig. 9 showed the temperature coefficients of the dielectric constant of SrCuSi$_4$O$_{10}$ ceramics sintered at 900 °C as a function of the TiO$_2$ content. When the content of TiO$_2$ was increased, the τ_ε value was observed to decrease from 38.60 to -15.40 ppm/°C. Furthermore, a near zero τ_ε value (1.80 ppm/°C) in this system was obtained when the SrCuSi$_4$O$_{10}$-1.0 wt% LiF samples added with 21 wt% TiO$_2$. As we known, the τ_ε value of the ceramics was greatly related to the composition of the ceramics. According to the study above, the SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramics with y wt% TiO$_2$ possessed positive τ_ε values and negative τ_ε values. Therefore, the τ_ε value in this system could be effectively adjusted from positive to negative by changing the content of TiO$_2$.
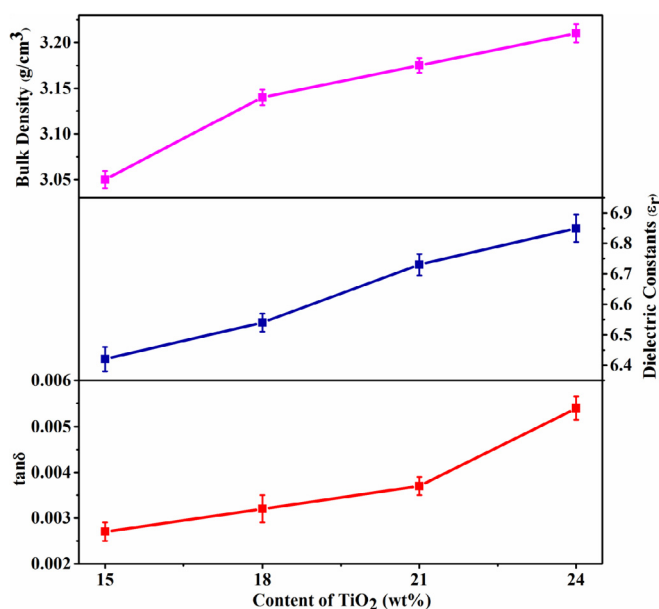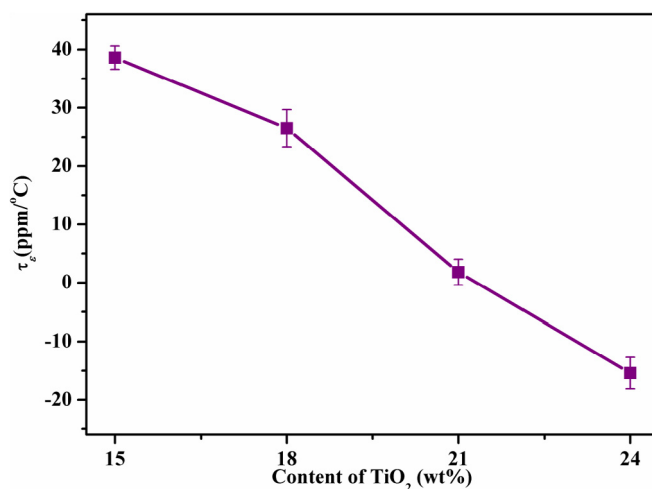
4. Conclusion

In this study, the effects of LiF addition on the sintering behaviors and dielectric properties of SrCuSi$_4$O$_{10}$ ceramic sintered at low temperature were investigated. And the sintering temperature of SrCuSi$_4$O$_{10}$ ceramics reduced to 900 °C from 1100 °C added with 1.0 wt % LiF. The main peak (202) exhibited a slight shift toward the higher 2θ degrees with increasing LiF addition due to the substitution of the F$^-$ ion in the O^{2-} sites. The behaviors of the bulk density of SrCuSi$_4$O$_{10}$ ceramics were associated with the sintering temperature and the amount of LiF. And the ε_r was dependent on the bulk density. The tanδ values were mainly affected by the extrinsic losses (densification and grain boundaries). Typically, excellent dielectric properties with $\varepsilon_r \sim 5.88$, $tan\delta \sim 1.6 \times 10^{-3}$ and $\tau_\varepsilon \sim 119.90$ ppm/°C were obtained for SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramics sintered at 900 °C. On this basis, τ_ε could be effectively modified to near zero by changing the TiO$_2$ content in SrCuSi$_4$O$_{10}$-1.0 wt% LiF ceramics and a stable two-phase system SrCuSi$_4$O$_{10}$-TiO$_2$ was formed. When the content of TiO$_2$ was increased from 15 to 24 wt%, the τ_ε decreased from 38.60 to -15.40 ppm/°C.

Addition of 21 wt% TiO_2 effectively improved the temperature stability of ceramics and τ_ε was adjusted to near zero. $SrCuSi_4O_{10}$-1.0 wt% LiF-21 wt% TiO_2 ceramics exhibited good dielectric properties of $\varepsilon_r \sim 6.73$, $\tan\delta \sim 3.7 \times 10^{-3}$ and $\tau_\varepsilon \sim 1.80$ ppm/°C when sintered at 900 °C for 6 h.

Acknowledgment

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