Enhanced Microwave Dielectric Properties and Sintering Behaviors of Mg$_2$SiO$_4$-Li$_2$TiO$_3$-LiF Ceramics by Adding CaTiO$_3$ for LTCC and GPS Antenna Applications

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Abstract: Mg$_2$SiO$_4$ holds promise for its application in the microwave communication field due to its low dielectric constant and high $Q\times f$ value. However, its high negative $\tau_f$ and high sintering temperature limit its application in low-temperature co-fired ceramic (LTCC) devices. In this work, Li$_2$TiO$_3$ and CaTiO$_3$ were introduced to improve the $\tau_f$, and LiF was chosen to decrease the sintering temperature. According to XRD patterns and SEM micrographs, the ceramic systems displayed a complex-phase structure, and the microstructure was densified when CaTiO$_3$ was added. All of the relative densities, dielectric constants, and $Q\times f$ values first increased and then decreased as the sintering temperature increased. The MLLC11.5 ceramics sintered at 800 $^\circ$C could be obtained with the highest $Q\times f$ value of 54,581 GHz (at 8.06 GHz), $\varepsilon_r$ of 14.13, and $\tau_f$ of +5.81 ppm/$^\circ$C. Furthermore, it was proven that the MLLC11.5 powders could be co-fired without any reaction with Ag powders at 800 $^\circ$C, indicating its potential for LTCC application. The MLLC11.5 composition was used to prepare a GPS antenna and showed good prospects for its application in electronic communications.

Keywords: Mg$_2$SiO$_4$-Li$_2$TiO$_3$-LiF-CaTiO$_3$ ceramics; structure; microwave dielectric property; LTCC; antenna

1. Introduction

As a multilayer ceramic manufacturing technology, low-temperature co-fired ceramic (LTCC) technology enables fabricating multilayer circuit boards and embedding passive devices with negligible packaging costs. Additionally, the devices tend to be smaller, thinner, and lighter due to the three-dimensional package. The conditions of large current and high-temperature resistance can also be satisfied by LTCC technology, contributing to the optimization of the thermal design of electronics. Catering to LTCC application, the ceramics must have a low dielectric constant ($\varepsilon_r < 15$), a high quality factor ($Q\times f$), and a near-zero temperature coefficient of resonant frequency ($\tau_f \sim +10$ ppm/$^\circ$C), which can guarantee the LTCC devices have high-frequency and high-speed transmission performance. Therefore, developing ceramics with excellent microwave dielectric properties (MWDPs) and lower sintering temperatures than the melting point of Ag (~961 $^\circ$C) has become one of the most important topics in the research of microwave dielectric materials.

A lot of low-dielectric materials have been reported, such as Silicates [1–4], tungstates [5–7], germanates [8–12], borates [13], molybdates [14], phosphates [15,16], and some oxides [17,18]. Among them, Mg$_2$SiO$_4$, which exhibits excellent MWDPs ($\varepsilon_r = 6–7$, $Q\times f = 240,000$ GHz) [19], is suitable for fabricating LTCC devices. Nevertheless, the negative and large $\tau_f$ ($\sim -60$ ppm/$^\circ$C)
and the high sintering temperature (≥1350 °C) of Mg2SiO4 weaken the frequency stability of the devices and limit their application in the LTCC field. Many studies have reported that the τf of Mg2SiO4 ceramics can be improved by doping ions [20,21] or adding a compound with a large positive τf value, such as TiO2 [22,23], CaTiO3 [24], and Ca0.9Sr0.1TiO3 [25], but these compounds generally have a small Q×f value and often decrease the Q×f value of Mg2SiO4 ceramics. The poor sintering behavior and decreased Q×f value of Mg2SiO4 ceramics can be attributed to the metastable enstatite or protoenstatite (MgSiO3) secondary phases induced by the conventional solid-state method [26]. To solve these two problems, it has been proven that the phase of MgSiO3 can be restrained by increasing the content of MgO, leading to an improved Q×f value [26,27]. MgSiO3 can also be eliminated by a two-step sintering process and mechanical activation [28]. The high sintering temperature of Mg2SiO4 ceramics can be lowered by adding an additive with a low melting point, such as LiF [29], B2O3-Li2CO3-H3BO3 [24], low-melting-point glass [30,31], or Ba3(VO4)2 [32]. In other words, the MWDPs and sintering behaviors of Mg2SiO4 ceramics can be enhanced by adding additives, which often exist in the form of secondary phases.

In this work, Mg2SiO4-Li2TiO3-LiF ceramics were chosen as the research system, in which Li2O, TiO2 and LiF were introduced to improve the MWDPs and sintering behaviors, respectively, because Li2TiO3 has a high Q×f value (−66,000 GHz) and a positive τf value (+22.1 ppm/°C) [33], and LiF has a high Q×f value (−73,880 GHz) and a low melting point (−845 °C) [34]. Moreover, Li2TiO3 could form a limited solid solution with LiF, contributing to the densification of the ceramic system. Finally, the composition of (61 wt% Mg2SiO4-39 wt% Li2TiO3)-8 wt% LiF was selected, and the MWDPs and sintering behaviors were further improved by adding CaTiO3, and the optimized composition was demonstrated to enable LTCC and GPS antenna application.

2. Materials and Methods

Mg2SiO4 (MSO) powders were first synthesized by the conventional solid-state method with the raw materials of MgO (99.9%, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China) and SiO2 (99.99%, Shanghai Macklin Biochemical Co., Ltd., Shanghai, China) according to the Mg2SiO4 stoichiometric ratio calcined at different temperatures (1250 °C, 1300 °C, 1350 °C, and 1400 °C) for 3 h (61 wt% Mg2SiO4-39 wt% Li2TiO3)-8 wt% LiF-x wt% CaTiO3 ceramics (x = 0, 7.5, 8.5, 9.5, 10.5, and 11.5; MLL, MLLC7.5, MLLC8.5, MLLC9.5, MLLC10.5, and MLLC11.5 for short, respectively) were prepared by the conventional solid-state reaction process using the starting materials including the composite Mg2SiO4, Li2TiO3 (99%, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China), LiF (99.99%, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China) and CaTiO3 (99.5%, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China). The mixed powders were ball-milled in absolute ethyl alcohol for 24 h. After the slurry was dried, the homogeneous powders were obtained and pressed into pellets, approximately 12 mm in diameter and 6 mm in thickness using 200 MPa pressure and 5% PVA binder. When burning out the binder at 600 °C for 2 h, all the samples were sintered at 775 °C, 800 °C, 825 °C, and 850 °C for 4 h in air using a muffle. To verify LTCC application, 40 wt% Ag powders were mixed with the MLLC11.5 powders without sintering, using the magnetic stirring method in absolute ethyl alcohol for 8 h. After mixing well and drying, the homogeneous powders were sintered at 800 °C for 4 h. The MLLC11.5 green body was coated with silver slurry and then sintered at 800 °C for 4 h. The GPS antenna was designed using HFSS software and prepared using the screen-printing method.

The crystal structures and microstructures of all the samples were examined by X-ray diffraction (XRD, SmartLab 3 KW, Rigaku, Tokyo, Japan) and scanning electron microscopy (SEM, Regulus8100, Hitachi, Tokyo, Japan), respectively. The elemental analysis used energy-dispersive X-ray spectroscopy (EDS) included in the SEM. The volume densities
were obtained according to the Archimedes method, and the theoretical densities \( (D_l) \) were calculated according to Equation (1)

\[
D_l = 1 / \sum_{i=1}^{n} \rho_{wi} D_{li} \quad (n \geq 2)
\]  

(1)

where \( \rho_{wi} \) and \( D_{li} \) are the weight percentage and theoretical density of the \( i \)-th phase, respectively, estimated from the Rietveld refinement results. The relative density is the proportion of the volume density to the theoretical density. \( \varepsilon_r \) and \( Q \times f \) are evaluated at about 25 °C by a vector network analyzer (E8363B, Agilent, California, USA). The frequency range is about 8.06 GHz–8.55 GHz. \( \tau_f \) is calculated according to Equation (2) by measuring the resonant frequencies at 20 °C \( (f_{20}) \) and 80 °C \( (f_{80}) \). All the error bars were obtained from three groups of data.

\[
\tau_f = \frac{f_{80} - f_{20}}{f_{20}(80 - 20)} \times 10^6 \text{ (ppm/°C)}
\]

(2)

3. Results and Discussion

Figure 1 shows the XRD patterns of the MSO powders calcined at different temperatures. As can be seen from Figure 1a, the MSO phase (ICDD 01-074-0714) was discovered in all the samples, combined with the secondary phases identified as MgSiO\(_3\) and MgO, which decreased with the increase in calcining temperature, as shown in Figure 1b,c. The SiO\(_2\) phase was detected when the powders were calcined at temperatures more than 1250 °C. Thus, it was too troublesome to obtain the composition of the pure MSO phase by the conventional solid-state method, as the MgSiO\(_3\) phase and residual MgO phase always emerged, induced by a small amount of amorphous SiO\(_2\) at high temperatures [26]. When the calcining temperature increased, the residual MgO reacted with MgSiO\(_3\), leading to an increase in the MSO phase [26]. Considering many clumps in the MSO powders calcined at 1400 °C, the optimum calcining temperature was selected as 1350 °C for the MSO powders in this work.

![Figure 1. XRD patterns of the MSO powders calcined at different temperatures. (a) 10°–80°, (b) 26.5°–29.5°, and (c) 42.5°–43.25°.](image)

Figure 2a shows the XRD patterns of the MLLC ceramics sintered at 800 °C. A principal crystalline phase identified as Mg\(_2\)SiO\(_4\) (ICDD 01-074-0714) was detected for all the samples. The secondary phases could be identified as LiTiO\(_2\), SiO\(_2\), Li\(_2\)TiO\(_3\), Li\(_2\)MgSiO\(_4\), and CaTiO\(_3\). No LiF phase was discovered from the XRD patterns of the MLLC ceramics, which could be attributed to the solid solution formation between Li\(_2\)TiO\(_3\) and LiF [35]. Due to this solid solution, Li\(^+\) and F\(^-\) ions entered into Li\(_2\)TiO\(_3\) lattice and formed the LiTiO\(_2\) phase, which could also be produced in ceramic systems with an excess MgO content [36,37]. The
phases of MgSiO₃, MgO, and amorphous SiO₂ react with Li₂TiO₃, leading to the formation of Li₂MgSiO₄ and LiTiO₂, according to the following reactions:

\[
\begin{align*}
2\text{Li}_2\text{TiO}_3 + \text{MgO} + \text{SiO}_2 & \rightarrow \text{Li}_2\text{MgSiO}_4 + 2\text{LiTiO}_2 + \frac{1}{2}\text{O}_2 \uparrow \\
2\text{Li}_2\text{TiO}_3 + \text{MgSiO}_3 & \rightarrow \text{Li}_2\text{MgSiO}_4 + 2\text{LiTiO}_2 + \frac{1}{2}\text{O}_2 \uparrow
\end{align*}
\]

As shown in Figure 2a, the CaTiO₃ phase existed in the ceramic systems in the form of the secondary phase without reaction with other phases. Rietveld refinements using Fullprof software were introduced to confirm the weight percentage and the theoretical density of each phase in the MLL ceramic without CaTiO₃, as shown in Figure 2b. The ion occupancy was revised based on the crystal structures of Li₂MgSiO₄, SiO₂, Li₂TiO₃, LiTiO₂, and Mg₂SiO₄. The XRD pattern of the MLL ceramic displayed good refinement. The refinement result is shown in Table 1. The theoretical density of the MLL ceramic was calculated according to Equation (1), with a value of about 3.381 g/cm³. As CaTiO₃ could not react with the MLL, the theoretical densities of the MLLC ceramics could also be calculated according to Equation (1).

![XRD patterns of the MLLC ceramics sintered at 800 °C.](image)

**Figure 2.** (a) XRD patterns of the MLL ceramics sintered at 800 °C. (b) Rietveld refinement plots of the MLL ceramic.

| Phase          | Dₜ (g/cm³) | Vᵣ (×10⁶ pm³) | ρᵣ (wt%) | Rᵥ (%) | Rₚ (%) | χ² | D (g/cm³) |
|----------------|------------|----------------|----------|--------|--------|----|----------|
| Mg₂SiO₄        | 3.311      | 290.337        | 59.07    |        |        |    |          |
| LiTiO₂         | 4.068      | 70.890         | 24.18    |        |        |    |          |
| LiTiO₃         | 3.404      | 428.252        | 8.60     |        |        |    |          |
| Li₂MgSiO₄      | 2.575      | 336.059        | 6.27     |        |        |    |          |
| SiO₂           | 2.270      | 175.838        | 1.88     |        |        |    |          |

Rᵥ: reliability factor of weighted patterns; Rₚ: reliability factor of patterns; and χ²: goodness of fit.

**Table 1.** Rietveld refinement result of the MLL ceramic.

Figure 3 shows the SEM micrographs of the cross-sections of the MLLC ceramics sintered at 800 °C. No grain changes were discovered for any of the samples when increasing the CaTiO₃ content. Some pores were detected for the MLL ceramic, and a dense microstructure was detected for all the samples with CaTiO₃ additives, which indicated that CaTiO₃ additives could promote the densification of the MLLC ceramics. Figure 4 shows the SEM micrographs of the cross-sections of the MLLC9.5 ceramics sintered at different temperatures. The micrograph differences between Figure 4a–d could be due to the breaking of the ceramics, leading to different flatnesses. The grain size of the MLLC9.5 ceramic increased with the increase in the sintering temperature, and some pores were
observed in all the samples except for those sintered at 800 °C, indicating that 800 °C was the optimal sintering temperature of the MLLC ceramics.

Figure 3. SEM micrographs of the cross-sections of the MLLC ceramics sintered at 800 °C. (a) MLL, (b) MLLC7.5, (c) MLLC8.5, (d) MLLC9.5, (e) MLLC10.5, and (f) MLLC11.5.

Figure 4. SEM micrographs of the cross-sections of the MLLC9.5 ceramics sintered at different temperatures. (a) 775 °C, (b) 800 °C, (c) 825 °C, and (d) 850 °C.
Figure 5 shows the relative densities, volume densities, dielectric constants, $Q \times f_s$, and $\tau_s$ of the MLLC ceramics. All the relative densities, volume densities, dielectric constants, and $Q \times f$ values first increased and then decreased with the increase in the sintering temperature and achieved a maximum value in the samples sintered at 800 °C. When the sintering temperatures were higher than 800 °C, the air in the ceramics could not escape in time, and isolated pores remained trapped, resulting in higher porosity [38]. The dielectric constants and $Q \times f$ values changed with the relative densities, which indicated that porosity played an important role in the MWDPs. The dielectric constants also varied in the additive amount of CaTiO$_3$ content due to the high dielectric constant of CaTiO$_3$ ceramics (~162) [39]. After adding the CaTiO$_3$ additives, an obvious increase in the relative density, dielectric constant, and $Q \times f$ was observed for all the MLLC ceramics, revealing that the MWDPs were improved with the decrease in porosity. The $\tau_s$ of the MLLC ceramics sintered at 800 °C increased linearly with the increase in the CaTiO$_3$ content. The variation of $\tau_s$ could mainly be attributed to the CaTiO$_3$ content and described according to the Lichtenecker empirical rule

$$\tau_f = V_1\tau_{f1} + V_2\tau_{f2}$$

where $V_1$ and $V_2$ are the volume fractions and $\tau_{f1}$ and $\tau_{f2}$ are the $\tau_f$ value of each phase. The increase in the $\tau_f$ value could be due to the increased concentration of the CaTiO$_3$ phase, which was reported to have a high positive $\tau_f$ value of +859 ppm/°C [39]. A near-zero $\tau_f$ value of +5.81 ppm/°C was obtained for the MLLC11.5 ceramics sintered at 800 °C with an optimal $Q \times f$ value of 54,581 GHz (at 8.06 GHz) and a low $\varepsilon_r$ value of 14.13.

Figure 5. Relative densities, volume densities, and microwave dielectric properties of the MLLC ceramics. (a) Relative densities, (b) volume densities, (c) dielectric constants, (d) $Q \times f_s$, and (e) $\tau_s$ of all the samples sintered at 800 °C.
As seen from the XRD pattern of MLLC11.5-40wt%Ag powders sintered at 800 °C in Figure 6a, Ag powders could not react with MLLC11.5 powders and mainly existed in the form of the secondary phase. Figure 6b shows a SEM micrograph of the cross-section of the MLLC11.5 ceramic, whose surface was coated with silver slurry. The ceramic was co-fired at 800 °C for 4 h and displayed a clear interface between the solidified silver slurry and the ceramic, marked as a and b, respectively. Figure 6c,d show the elemental analysis results of areas a and b by EDS, which displayed that areas a and b belonged to Ag and the MLLC11.5 ceramic, respectively. This result indicates that MLLC11.5 ceramics could be suitable for LTCC application.

![Figure 6](image)

Figure 6. (a) XRD pattern of MLLC11.5-40 wt% Ag powders calcined at 800 °C, (b) SEM micrograph of the cross-section of MLLC11.5 ceramic coated with silver slurry and sintered at 800 °C, (c) EDS result of area a, and (d) EDS result of area b.

The MLLC11.5 composition was also employed to prepare a GPS antenna composed of a ground plane, radiation layer, and dielectric substrate. The designed sample is shown in Figure 7a. The dielectric substrate was the MLLC11.5 ceramic, about 1.5 mm thick and 21 mm in diameter. The radiation layer was a camber line with a 1 mm width, whose length could be modified to satisfy the GPS frequency (~1.575 GHz). Another part of the front face was the ground plane, which also included a part of the side face and half of the back face of the dielectric substrate. Considering the size limit of the dielectric substrate, the radiation layer could connect with the ground plane through a metal wire with 50 Ω impedance, which could increase the inductance of the antenna to reduce the resonant frequency. The GPS antenna was designed with HFSS software and prepared with the screen-printing process according to the designed size. The front and back face of the GPS antenna is shown in Figure 7b,c, respectively. The metal pattern of the side face was handmade. The soldering was guaranteed by thickening and widening the silver slurry of the solder joint position. Figure 7d shows the return loss (S11) of the GPS antenna. Both the simulated and experimental data of the S11 were less than −10 dB at the resonant frequency. By modifying the length of the radiation layer, the resonant frequency was improved and nearly identical to the simulated data. The GPS signal test was carried out for the antenna by using a hardware system and displayed in the software, as shown in Figure 7e. A total of 11 or 12 Pcs GPS satellites were detected at the same time and displayed more than a 28 dBHz carrier-to-noise ratio (C/N0) on average, indicating antenna application [40].
Figure 7. GPS antenna application. (a) Designed sample, (b) front face of the GPS antenna, (c) back face of the GPS antenna, (d) return loss (S11), (e) experimental process of GPS signal, and (f) C/N0 and number of satellites.

4. Conclusions

MLLC ceramics with different amounts of CaTiO3 additives were prepared using the conventional solid-state method. The effects of CaTiO3 contents on the structures, sintering behaviors, and MWDPs were studied. A mixed-phase structure composed of Mg2SiO4, LiTiO2, Li2TiO3, Li2MgSiO4, SiO2, and CaTiO3 was detected using the XRD pattern. The relative density significantly increased after adding CaTiO3, leading to a significantly increased $Q \times f$. The dielectric constant and $Q \times f$ first increased and then decreased with the increase in the sintering temperature, and achieved a maximum value when the MLLC11.5 ceramics were sintered at 800 °C with an $\varepsilon_r$ of 14.13 and $Q \times f$ of 54,581 GHz (at 8.06 GHz). The $\tau_f$ increased linearly with the increase in the CaTiO3 content and reached three near-zero values of $-5$, $+2.59$, and $+5.81$ ppm/°C for MLLC9.5, MLLC10.5, and MLLC11.5 compositions, respectively. The MLLC11.5 composition could be co-fired without any reaction with Ag powders at 800 °C, indicating LTCC application. In the investigation of the GPS antenna, the MLLC11.5 composition exhibited good potential for antenna application.

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