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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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 ($\tau_f \sim \pm 10$ ppm/°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 °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 $\tau_f$ (~−60 ppm/°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 Ca₀.₅Sr₀.₅TiO₃ [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], Bi₂O₃-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 Li₄TiO₃ 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 \( D_i \) were calculated according to Equation (1)

\[
D_i = 1 / \sum_{i=1}^{n} \frac{\rho_{\text{ti}}}{D_i}, (n \geq 2)
\]

where \( \rho_{\text{ti}} \) and \( D_i \) 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.

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

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 an increase in calcining temperature, as shown in Figure 1b,c. The SiO\(_2\) phase was detected when the powders were calcined at 1250 °C, while there was no SiO\(_2\) phase 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 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°.

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 Li$_2$TiO$_3$, 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 Li$_2$TiO$_3$ phase, which could also be produced in ceramic systems with an excess MgO content [36,37].
phases of MgSiO$_3$, MgO, and amorphous SiO$_2$ react with Li$_2$TiO$_3$, leading to the formation of Li$_2$MgSiO$_4$ and LiTiO$_2$, according to the following reactions:

$$2\text{Li}_2\text{TiO}_3 + \text{MgO} + \text{SiO}_2 \rightarrow \text{Li}_2\text{MgSiO}_4 + 2\text{LiTiO}_2 + \frac{1}{2}\text{O}_2 \uparrow$$  \hfill (3)

$$2\text{Li}_2\text{TiO}_3 + \text{MgSiO}_3 \rightarrow \text{Li}_2\text{MgSiO}_4 + 2\text{LiTiO}_2 + \frac{1}{2}\text{O}_2 \uparrow$$  \hfill (4)

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

As shown in Figure 2a, the CaTiO$_3$ 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 CaTiO$_3$, as shown in Figure 2b. The ion occupancy was revised based on the crystal structures of Li$_2$MgSiO$_4$, SiO$_2$, Li$_2$TiO$_3$, LiTiO$_2$, and Mg$_2$SiO$_4$. 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/cm$^3$. As CaTiO$_3$ could not react with the MLL, the theoretical densities of the MLLC ceramics could also be calculated according to Equation (1).

<table>
<thead>
<tr>
<th>Phase</th>
<th>$D_t$ (g/cm$^3$)</th>
<th>$V_t$ ($\times 10^6$ pm$^3$)</th>
<th>$\rho_t$ (wt%)</th>
<th>$R_{wp}$ (%)</th>
<th>$R_p$ (%)</th>
<th>$\chi^2$</th>
<th>$D$ (g/cm$^3$)</th>
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<tr>
<td>Mg$_2$SiO$_4$</td>
<td>3.311</td>
<td>290.337</td>
<td>59.07</td>
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<tr>
<td>LiTiO$_2$</td>
<td>4.068</td>
<td>70.890</td>
<td>24.18</td>
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<tr>
<td>LiTiO$_3$</td>
<td>3.404</td>
<td>428.252</td>
<td>8.60</td>
<td>13.9</td>
<td>9.82</td>
<td>5.42</td>
<td>3.381</td>
</tr>
<tr>
<td>Li$_2$MgSiO$_4$</td>
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<td>336.059</td>
<td>6.27</td>
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<tr>
<td>SiO$_2$</td>
<td>2.270</td>
<td>175.838</td>
<td>1.88</td>
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$R_{wp}$: reliability factor of weighted patterns; $R_p$: reliability factor of patterns; and $\chi^2$: goodness of fit.

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 CaTiO$_3$ content. Some pores were detected for the MLL ceramic, and a dense microstructure was detected for all the samples with CaTiO$_3$ additives, which indicated that CaTiO$_3$ 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. 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) \( \tau f_s \).
Figure 5 shows the relative densities, volume densities, dielectric constants, $Q \times f_s$, and $\tau_f$ 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 $\tau_f$ of the MLLC ceramics sintered at 800 °C increased linearly with the increase in the CaTiO$_3$ content. The variation of $\tau_f$ 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) $\tau_f$ of all the samples sintered at 800 °C.
As seen from the XRD pattern of MLLC11.5-40 wt% 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. (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 CaTiO$_3$ additives were prepared using the conventional solid-state method. The effects of CaTiO$_3$ contents on the structures, sintering behaviors, and MWDPs were studied. A mixed-phase structure composed of Mg$_2$SiO$_4$, LiTiO$_2$, Li$_2$TiO$_3$, Li$_2$MgSiO$_4$, SiO$_2$, and CaTiO$_3$ was detected using the XRD pattern. The relative density significantly increased after adding CaTiO$_3$, 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 CaTiO$_3$ 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.

Author Contributions: Conceptualization, Z.W. and Y.C.; methodology, Z.W. and F.P.; validation, Z.W. and Y.C.; investigation, Z.W., F.P. and L.L.; resources, Y.C.; data curation, Z.W. and Y.C.; writing—original draft preparation, Z.W.; writing—review and editing, Z.W., Q.D., R.T. and Y.C.; visualization, J.A. and H.Z.; supervision, Y.C.; project administration, Y.C.; and funding acquisition, Y.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Zhejiang Province Key Research and Development Project (Grant Nos. 2019C05002, 2020C05004, 2021C01183), National Natural Science Foundation of China (Grant No. 11902292), Postdoctoral Program of Zhejiang Province (Grant No. ZJ2020018), National Natural Science Foundation of Zhejiang Province (Grant Nos. LQ20E030008, LQ20E050014, LQ20A020005, LGG20E050011) and National Key Research and Development Program of China (Grant No. 2020YFC2007101).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.


