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Sintering behavior and microwave dielectric properties of Li_2O–B_2O_3–SiO_2 doped $MgTiO_3$–$CaTiO_3$ ceramics

Yang Wang[1] · Ruzhong Zuo[1] · Jian Zhang[1] · Shishun Qi[1] · Tianwen Zhang[1]

Abstract The influence of the addition of low-melting point Li_2O–B_2O_3–SiO_2 (LBS) on the sintering behavior and microwave dielectric properties of commercial $0.95MgTiO_3$–$0.05CaTiO_3$ (95MCT) was systematically investigated by means of an X-ray diffractometer, a scanning electron microscope and a network analyzer. The results revealed that the addition of an appropriate amount of LBS enables the 95MCT composite ceramic to sinter in an obviously low sintering temperature, simultaneously leading to a more uniform and compact microstructure. Furthermore, favorable microwave dielectric properties of $\varepsilon_r = 18.2$, Qxf = 67,000 GHz (7.9 GHz), $\tau_f = -5.2$ ppm/°C) were yielded in the 10 wt% LBS-doped 95MCT sample when sintered at 1025 °C for 4 h, indicating that LBS is an effective ternary firing agent when employed in 95MCT system. The relatively low sintering temperature together with acceptable microwave dielectric properties enable the composite ceramic to be a more potential alternative for the present patch antennas.

1 Introduction

The advances in microwave telecommunication, satellite broadcasting and intelligent transport systems over the past decades have resulted in an increasing demand for dielectric resonators, which are low-loss ceramic pucks used mainly in wireless communication systems [1]. Requirements for these dielectrics must be combined with a high dielectric constant ($\varepsilon_r > 15$) for possible size miniaturization, a low dielectric loss (Q > 5000, where Q = 1/tanδ) for high frequency selectivity and low signal attenuation and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stable circuit. As a representative of microwave dielectric materials, magnesium titanate ($MgTiO_3$) has been increasingly popular and widely applied in large dimensional resonators, global system position (GPS) antennas and filters. Its microwave dielectric properties ($\varepsilon_r = 17$, Qxf = 160,000 GHz, $\tau_f = -50$ ppm/°C) are usually adjusted by introducing $CaTiO_3$ ($\varepsilon_r = 170$, Qxf = 3600 GHz, $\tau_f = +800$ ppm/°C) to obtain a nero-zero τ_f value [2, 3]. $MgTiO_3$–$CaTiO_3$ (MCT) composite ceramic is well known as the material for temperature compensating type capacitor, dielectric resonator and patch antenna. Good microwave dielectric properties of $\varepsilon_r = 20$, Qxf = 60,000 GHz, $\tau_f = 0$ ppm/°C can be obtained when the $0.95MgTiO_3$–$0.05CaTiO_3$ (in molar ratio) ceramic (hereafter referred to as 95MCT) was sintered at 1400–1450 °C.

However, its high sintering temperature makes it costly as it is employed in practical applications. Moreover, $MgTi_2O_5$ usually appears as a secondary phase during the fabrication of MCT composite ceramics, which inevitably sacrifices dielectric properties of the matrix [4]. In general, doping low-melting point glass, chemical processing and the use of fine starting powders are effective ways in reducing the sintering temperature of dielectric materials [5–10]. It has been demonstrated that the liquid-phase sintering by adding glass phases will definitely deteriorate the microwave dielectric properties and the chemical process often requires a flexible procedure, which is expensive and time consuming. Thus, researches have been extensively conducted to lower the sintering temperature of the MCT

✉ Ruzhong Zuo
piezolab@hfut.edu.cn; rzzuo@hotmail.com

[1] Institute of Electro Ceramics and Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, People's Republic of China

ceramics by using different kinds of low-melting point additives such as Bi_2O_3, $3ZnO–2Nb_2O_5$, Co2O3, B_2O_3 (glass), $ZnO–ZrO_2$ and $BaCu(B_2O_5)$ [11–16]. However, the firing temperature for the obtained composite is still too high for actual production.

Some composite oxides, such as $ZnO–B_2O_3–SiO_2$ (ZBS) [17], $Li_2O–V_2O_5$ [18] and $Li_2O–B_2O_3–SiO_2$ (LBS) [19], have been demonstrated as effective sintering aids. For example, the sintering temperature of $BaTiO_3$ could be significantly lowered from 1300 to 900 °C by introducing ZBS [17]. Jantunen et al. [20] investigated the microwave dielectric properties of ZBS-doped MCT composite ceramics through a prior glass preparation. Though the samples were densified at only 900 °C when ZBS was mixed with MCT in a weight ratio of 7:3, yet seriously deteriorated microwave dielectric properties of $\varepsilon_r = 10.6$, Q = 880 GHz (∼7 GHz) were yielded. Similarly, Shin and Shin [19] systematically investigated the phase evolution, sintering behavior and microwave dielectric properties of LBS-doped $0.9MgTiO_3–0.1CaTiO_3$ (90MCT) ceramics, in which a prior glass preparation was also conducted before LBS was added to the matrix. The samples experienced a complicated phase evolution during firing and the 10 wt% LBS glass-added specimen demonstrated a dielectric permittivity of $\varepsilon_r = 19.1$, a much lower Qxf of 13,000 GHz, and a τ_f of −1.3 ppm/°C as it was fired at 950 °C for 2 h.

In this paper, we managed to combine 95MCT and low-melting point LBS oxides to construct a composite system with favorable microwave dielectric properties under a relatively low sintering temperature. The effects of the LBS addition on the densification, microstructure and microwave dielectric properties of 95MCT ceramics were explored in detail.

2 Experimental procedure

Samples of $MgTiO_3$ and $CaTiO_3$ were individually synthesized by a conventional solid-state method from high-purity powders of MgO, $CaCO_3$ and TiO_2. Firstly, MgO and TiO_2 were mixed in a molar ratio of 1.04:1, stoichiometric amounts of $CaCO_3$ and TiO_2 powders were weighed, and the above two powder mixtures were ball-milled in distilled water for 4 h using zirconia balls, and then calcined at 1150 and 1250 °C for 4 h after drying, respectively. The calcined powders were mixed together according to the formula of $(1 − x)MgTiO_3–xCaTiO_3$ (x = 0.04, 0.05, 0.06, 0.07 mol, xMCT), and then re-milled for 6 h together with 5 wt% PVA binder. LBS, which was composed of Li_2CO_3, B_2O_3 and SiO_2 in a weight ratio of Li_2CO_3:B_2O_3:SiO_2 = 3:6:1, was directly added to 95MCT according to the formula of 95MCT–y wt% LBS

(y = 5, 10, 20) and then ball-milled again for 6 h. The granulated powders were subsequently pressed into cylinders with dimensions of 10 mm in diameter and 7–8 mm in height. The specimens were first heated at 550 °C in air for 4 h to remove the organic binder and then sintered at 1300–1460 °C for 4 h (xMCT) and 900–1100 °C for 4 h (for 95MCT–y wt% LBS), respectively.

The bulk densities of the sintered pellets were evaluated using the Archimedes method. The crystal structures of the fired ceramics were identified via an X-ray diffractometer (XRD, D/Max2500 V, Rigaku, Japan) using CuKα radiation. The microstructure of the pellets was observed by a scanning electron microscope (SEM, JSM-6490LV, JEOL, Tokyo, Japan). Microwave dielectric properties of the sintered ceramics were measured using a network analyzer (N5230C, Agilent, Palo Alto, CA) and a temperature chamber (GDW-100, Saiweisi, Changzhou, China). The τ_f values of the samples were measured in the temperature range from 20 to 80 °C and calculated by the following equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3 Results and discussion

Figure 1 provides the XRD patterns of the calcined $MgTiO_3$ and $CaTiO_3$ powders, the sintered xMCT and 95MCT–y wt% LBS powders at various temperatures for 4 h. It is obvious that a suitable molar ratio of
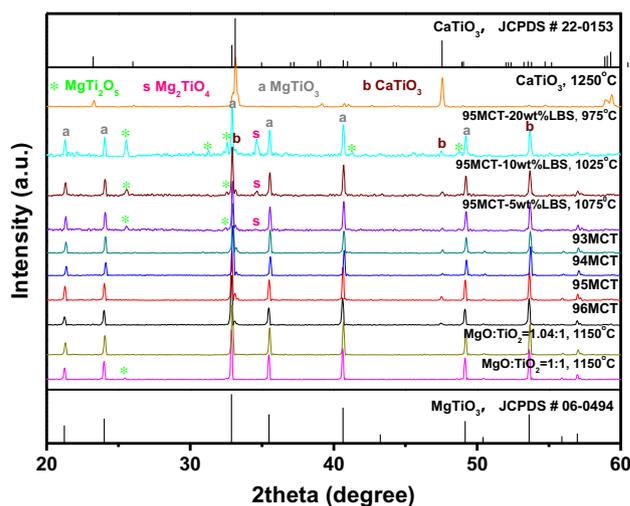
Fig. 1 XRD patterns of the calcined $MgTiO_3$ and $CaTiO_3$ powders, the xMCT and 95MCT–y wt% LBS ceramics sintered at various temperatures for 4 h

$MgO:TiO_2 = 1.04:1$ can effectively avoid the formation of $MgTi_2O_5$, which usually appeared as a secondary phase in MCT samples. Pure phase $MgTiO_3$ and $CaTiO_3$ could be obtained when they were calcined at 1150 and 1250 °C, respectively. As for the xMCT (x = 0.04, 0.05, 0.06, 0.07 mol) samples sintered at 1340 °C, it can be seen that $MgTiO_3$ and $CaTiO_3$ coexisted well without any additional phases regardless of the variation of x, indicating the formation of typical MCT composite ceramics. Also, the XRD patterns of 95MCT–y wt% LBS (y = 5, 10, 20) samples sintered at their respective optimum temperatures are displayed in Fig. 1. $MgTi_2O_5$ and Mg_2TiO_4 appeared as secondary phases simultaneously when LBS was added to the matrix, and the peak intensities of the two phases increased with increasing amount of LBS. The following reaction processes might be responsible for the appearance of $MgTi_2O_5$ and Mg_2TiO_4:

$$2MgTiO_3 = Mg_2TiO_4 + TiO_2 \tag{2}$$

$$2MgTiO_3 = MgTi_2O_5 + MgO \tag{3}$$
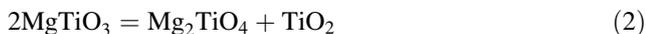
Of particular note is that the peak intensity of $MgTiO_3$ did not demonstrate an obvious decrement. Meanwhile, there were no detectable peaks of MgO and TiO_2. The reason for this seemed to be associated with the reaction between MgO and TiO_2, after which $MgTiO_3$ was formed again. The formation and decomposition process of $MgTiO_3$ seemed to proceed synchronously as discussed above. However, the two detected secondary phases did not react to form the main phase $MgTiO_3$ as the following equation proceeded:

$$Mg_2TiO_4 + MgTi_2O_5 = 3MgTiO_3 \tag{4}$$
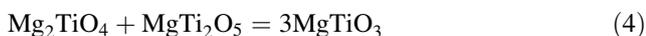
The reason for this seemed to be associated with the fact that the reaction temperature for Eq. (4) exceeded the current temperature of 95MCT–y wt% LBS system, thus leading to the residual of Mg_2TiO_4 and $MgTi_2O_5$.

Figure 2 gives the SEM images of 95MCT and 95MCT–y wt% LBS samples sintered at their respective temperature range. For the fired 95 MCT ceramics, as can be seen from Fig. 2a–c, the large grains were identified as $MgTiO_3$, containing dispersed small $CaTiO_3$ crystallites inside, small particles scattered along grain boundaries were also $CaTiO_3$. As expected, $MgTiO_3$ and $CaTiO_3$ phases were virtually separated since there was no solubility between them because of the different crystal structures. As the sintering temperature increased, the microstructure of 95MCT gradually became denser, there were only few pores in the compactly packed grains after sintering at 1340 °C for 4 h. A further increment in sintering temperature resulted in abnormal grain growth and a more porous microstructure was thus observed. The microstructure images of 95MCT sintered at various

temperatures for 4 h with varying amounts of LBS are displayed in Fig. 2d–h. When compared with the 5 wt% LBS-added sample sintered at 1075 °C, which can be observed in Fig. 2d, the microstructure became more denser and uniform when the 10 wt% LBS was added, as displayed in Fig. 2e. A further increase of x content would definitely result in an inhomogeneous and porous microstructure, as can be seen from Fig. 2h. Thus, by adding appropriate amount of LBS, the densification behavior could be effectively enhanced under a much lower temperature. As for the 95MCT–10 wt% LBS samples, the grain size increased continuously with the increase of sintering temperature, which are displayed in Fig. 2e–g. For liquid sintering of ceramics, the liquid phase would be resident or disappear in the final stage. The pores were almost eliminated for the specimen sintered at 1025 °C due to the effect of liquid phase and the grain grew rapidly above 1075 °C. It also revealed non-uniform grain morphology.

Figure 3 depicts the variation of relative density, ε_r and Qxf value of xMCT ceramics as a function of sintering temperature. As the sintering temperature increased, the relative density increased firstly and then dropped after reaching their maximum values. All the samples possessed rather high relative density (>95 %), suggesting a good densification behavior. With respect to the microwave dielectric properties of MCT samples, the variation of ε_r and Qxf value as a function of sintering temperature exhibited similar trends to that of relative density, since the density and ε_r of a ceramic are associated with the elimination of pores. And the improvement in Qxf was mainly attributed to the increment in densification. With the elimination of the secondary phase Mg_2TiO_5 ($\varepsilon_r = 17.4$, Qxf = 47,000 GHz, $\tau_f = -66$ ppm/°C) [19], the $0.96MgTiO_3$–$0.04CaTiO_3$ (96MCT) ceramic sintered at 1340 °C for 4 h exhibited a much higher Qxf value of 101,835 GHz (8.1 GHz) than previous report [13]. Table 1 lists the microwave dielectric properties of the xMCT ceramic system sintered at 1340 °C for 4 h. As the x increased from 0.04 to 0.07, ε_r increased and Qxf decreased monotonously, τ_f values shifted towards positive direction and a near-zero τ_f could be achieved by adjusting the amount of $CaTiO_3$ content reasonably. The variation tendency was consistent with the mixing rule.

To lower the sintering temperature and maintain comparable microwave dielectric properties of MCT composite ceramics, various amounts of LBS were employed as sintering agents. Relative density was determined by assuming no chemical reactions occur between the formed LBS glass phase and the matrix material in order to roughly estimate the degree of densification. The 95MCT samples doped with a relatively large amount of LBS were sintered at lower temperatures than other ceramics (5, 10 wt%), probably because of an obvious effect of liquid phase
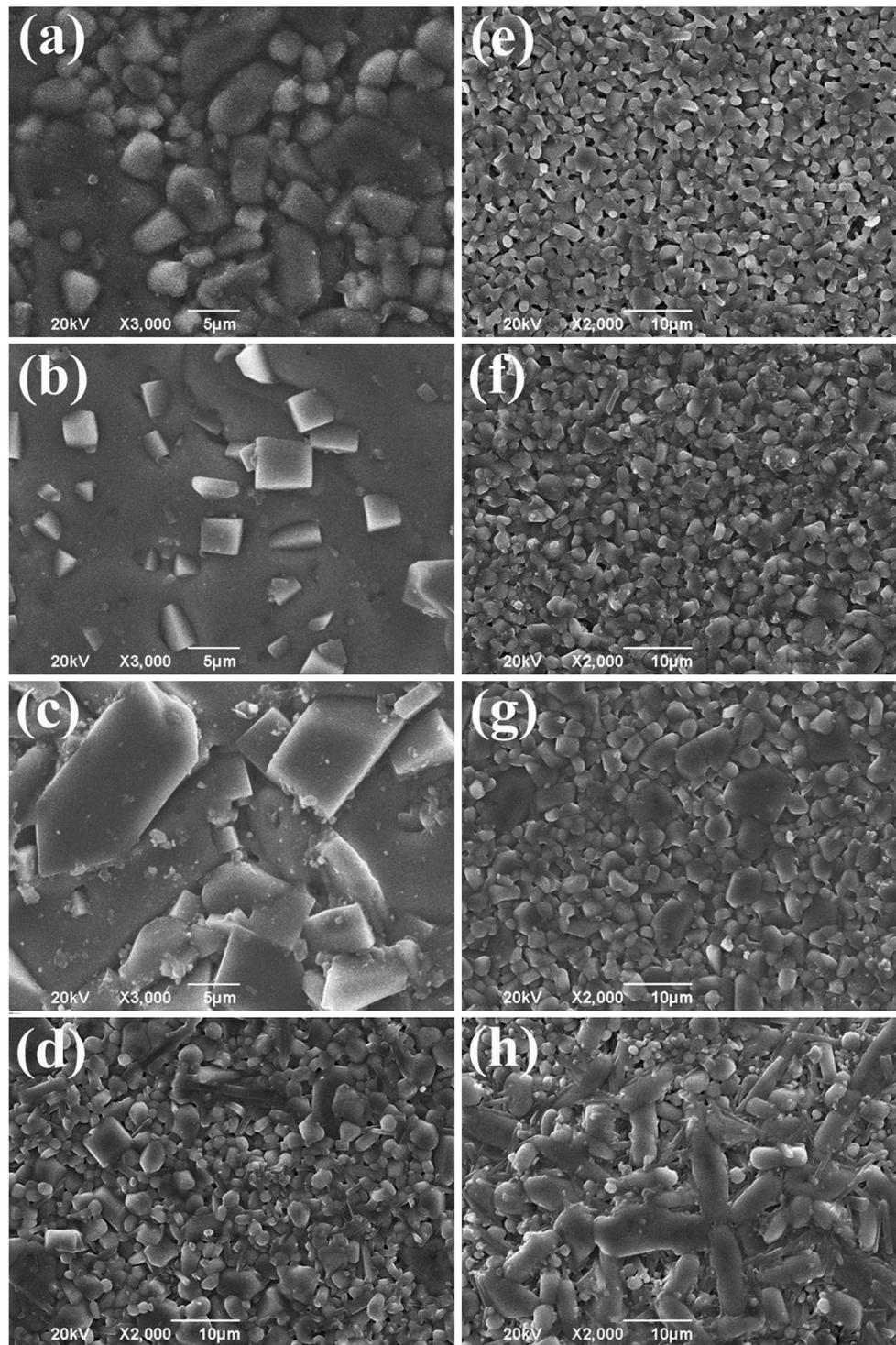
Fig. 2 SEM images of the 95MCT samples sintered at **a** 1300 °C, **b** 1340 °C, **c** 1380 °C for 4 h, the 95MCT–5 wt% LBS sample sintered at **d** 1075 °C, the 95MCT–10 wt% LBS samples at **e** 1000 °C, **f** 1025 °C, **g** 1075 °C, and the 95MCT–20 wt% LBS sample at **h** 975 °C for 4 h

sintering, as can be clearly seen from Fig. 4, which can promote the sintering process under lower temperature. The existence of liquid phase might be associated with the low-melting point of LBS. In addition, considering the

overall dielectric properties of MCT samples, the 95MCT with a pretty good Qxf value and a near-zero τ_f was chosen as the matrix. Figure 4 shows the variation of relative density and ε_r of MCT–y wt% LBS ceramics as a function
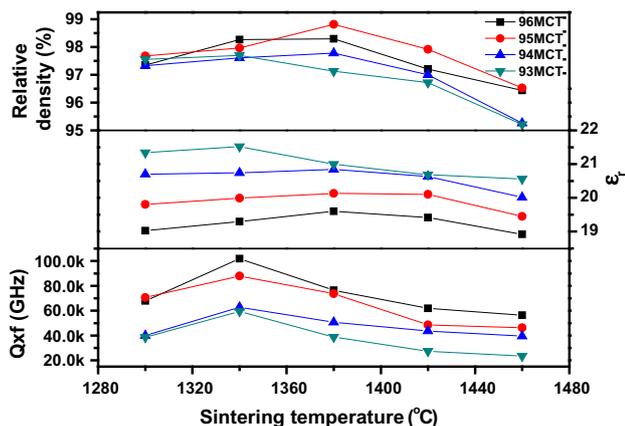
Fig. 3 The variation of relative density, ε_r and Qxf value of xMCT ceramics as a function of sintering temperature

Table 1 Microwave dielectric properties of xMCT (x = 0.04, 0.05, 0.06, 0.07) ceramics sintered at 1340 °C for 4 h

x	ε_r	Qxf (GHz)	τ_f (ppm/°C)
0.04	19.3	101,835	−9.4
0.05	20	87,935	−3.5
0.06	20.7	62,784	−0.3
0.07	21.5	59,388	+6.8
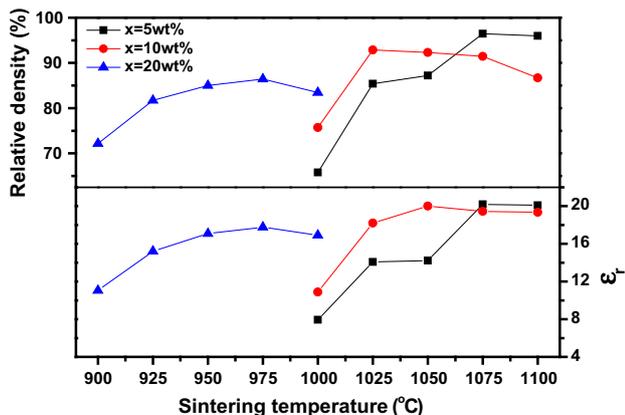
Fig. 4 The variation of relative density and ε_r of 95MCT–y wt% LBS ceramics with changing sintering temperatures for 4 h

of sintering temperature. It can be seen that 1075 °C seemed to be sufficient for the appropriate densification of 5 wt% LBS-added specimens. For 10 and 20 wt% LBS-added specimens, acceptable densification were achieved at 1025 and 975 °C, respectively. Considering the fact that pure MCT ceramic required a sintering temperature above 1340 °C, the addition of glass-forming oxides LBS in this work significantly lowered the sintering temperature. The ε_r of LBS-doped specimens showed decreased values when

compared with those of pure 95MCT, in proportional to the amount of LBS. This decrement seemed to be natural as the permittivity of the LBS (ε_r = 7.97) is lower than that of 95MCT (ε_r = 20). For the case of 5 wt% LBS specimens, especially sintered at temperatures lower than 1025 °C, the permittivity was even lower than 10 and 20 wt% LBS specimens although the additive addition was minimal. The presence of pores in this specimen because of the poor densification at low temperatures was believed to yield such behavior.

Figure 5 illustrates the variation in Qxf of 95MCT doped with varying amounts of LBS as a function of sintering temperature. The decrease of the Qxf of the 5 and 10 wt% specimens below 1075 and 1025 °C was also correlated with the poor densification. A significant improvement of Qxf value was observed in the 5 and 10 wt% LBS-doped samples when sintered at 1075 and 1025 °C for 4 h, respectively, which can be attributed to the promoted grain growth and densification of 95MCT. With further increment of the sintering temperature, slightly decrease of Qxf values were achieved, probably owing to the over sintering and abnormal grain growth. However, 20 wt% LBS seemed to be excess for the 95MCT matrix as they generally obtained rather low Qxf values. Combined this kind of variation with that of relative density, it could be concluded that lower density would necessarily resulted in lower Qxf values. Inset of Fig. 5 shows the variation of τ_f values as a function of x content. With increasing x content, τ_f tended to shift to a more negative direction. Table 2 gives a comparison of microwave dielectric properties of some typical MCT ceramics with different additives. It can be seen that with 10 wt% LBS added to the 95MCT sample, lower sintering temperature together with superb
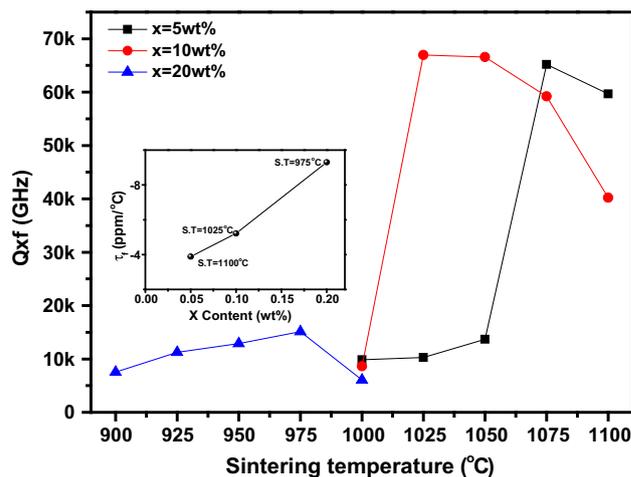
Fig. 5 The variation of Qxf value of the 95MCT–y wt% LBS ceramics sintered at different temperatures for 4 h; the *inset* shows the τ_f variation of 95MCT doped with different amounts of LBS

Table 2 The comparison of microwave dielectric properties for some typical MCT composite ceramics with different additives

Ceramics	ST (°C)	ε_r	Qxf (GHz)	τ_f (ppm/°C)	Ref.
95MCT–1 mol% Co_2O_3	1300	20.5	76,485	+2.43	[13]
95MCT–3 wt% $BaCu(B_2O_5)$	1100	21.5	28,000	−3.3	[16]
95MCT–5 wt% B_2O_3 (glass)	1050	17.2	22,000	−1.6	[14]
95MCT–0.25 wt% ($3ZnO–2Nb_2O_5$)	1320	20.3	72,730	−6.8	[12]
95MCT–1 wt% ZnO–0.5 % WO_3	1310	20.2	62,000	−5.1	[21]
90MCT–10 wt% LBS (glass)	950	19.1	13,000	−1.3	[19]
95MCT–10 wt% LBS (mixed oxides)	1025	18.2	67,000	−5.2	This work

ST sintering temperature, *Ref.* references

microwave dielectric properties can be achieved, which indicates that the ternary sintering aid LBS is effective when introduced to the 95MCT system. Moreover, the experimental process left out the preparation of LBS glass.

4 Conclusions

In this work, pure-phase $MgTiO_3$ was successfully prepared by reasonably adjusting the molar ratio of MgO and TiO_2 to avoid the formation of secondary phase $MgTi_2O_5$. The as-prepared 95MCT composite ceramic without any impurities exhibited good microwave dielectric properties of $\varepsilon_r = 20$, Qxf = 87,935 GHz (8 GHz), $\tau_f = -3.5$ ppm/°C when sintered at 1340 °C for 4 h. The ternary sintering aid LBS was employed to lower the firing temperature of MCT ceramics. With increasing amount of LBS, the 95MCT samples experienced a significant reduction in densification temperature. Meanwhile, excellent microwave dielectric properties of $\varepsilon_r = 18.2$, Qxf = 67,000 GHz (7.9 GHz), $\tau_f = -5.2$ ppm/°C were obtained in the 10 wt% LBS-doped 95MCT ceramic when sintered at 1025 °C for 4 h. The overall results demonstrate that 95MCT doped with 10 wt% LBS would be a promising microwave dielectric material for the application of GPS antennas.

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