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Short communication

Low-loss and low-temperature firable $Li_2Mg_3SnO_6$-$Ba_3(VO_4)_2$ microwave dielectric ceramics for LTCC applications

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ABSTRACT

A new low-loss and low-temperature fired $(1-x)Li_2Mg_3SnO_6$-$xBa_3(VO_4)_2$-3 wt% LiF ($(1-x)L_2MS$-xBV-$0.03LiF$) ceramic was prepared *via* a conventional solid-state route. The results indicate that L_2MS and BV phases can stably coexist in the composite up to at least 900 °C. The appearance of a secondary phase $Li_4MgSn_2O_7$ at temperatures lower than 800 °C was ascribed to the low-temperature decomposition of L_2MS, irrespective of the existence of BV or LiF. Microwave dielectric properties of L_2MS-BV composites generally displayed a nearly linear relation with x and obeyed a well-known mixing rule. With the help of 3 wt% LiF, the $x = 0.37$ sample sintered only at 850 °C for 6 h exhibited excellent microwave dielectric properties of $\varepsilon_r = 12.8$, $Q \times f =$ 101,705 GHz (@ 9.64 GHz) and near-zero τ_f of −2.9 ppm/°C. The good chemical compatibility with Ag further indicates that the $0.63L_2MS$ – $0.37BV$-$0.03LiF$ composite ceramic would be a promising dielectric material for low temperature co-fired ceramic applications.

1. Introduction

Low-temperature co-fired ceramic (LTCC) technology has become crucial for modern wireless communication system, which requires dielectric materials to own low sintering temperatures, excellent chemical compatibility with Ag electrode, near-zero temperature coefficient of resonant frequency (τ_f), high quality factor ($Q \times f > 5000$ GHz) and appropriate dielectric constant (ε_r) [1,2]. A lot of research work has been focused on developing new low-loss LTCC materials with excellent performances [3,4].

Rock salt-structured $Li_2Mg_3BO_6$ (L_2MB, B = Ti, Sn, Zr) ceramic system has attracted extensive attention in recent years owing to its ultra-low loss [5–7]. L_2MB (B = Ti, Sn, Zr) ceramics sintered at 1280, 1360 and 1380 °C possessed excellent microwave dielectric properties of $\varepsilon_r = 15.2$, 8.8 and 12.6, $Q \times f = 152{,}000$, 123,000 and 86,000 GHz, and $\tau_f = -39$, -32 and -36 ppm/°C, respectively [5]. However, the porous microstructure and secondary phases caused by lithium evaporation have significantly deteriorated their microwave dielectric properties. The pure-phase L_2MB ceramics could be prepared by means of atmosphere controlled sintering through burying the sample pellets in sacrificial powder of the same composition. As a result, greatly enhanced $Q \times f$ values of 110,000–300,000 GHz were attained in well-sintered ceramics [6,7]. The outstanding microwave dielectric properties have highlighted their enormous potentials, but the high sintering temperature and large τ_f values have hindered their practical applications. A near-zero τ_f value was reported in $Li_2Mg_3TiO_6$ ceramics with the addition of $Ca_{0.8}Sr_{0.2}TiO_3$ or the substitution of 12% Ca for Mg, resulting from the secondary phase with an opposite-sign τ_f value [8–10]. However, $CaTiO_3$ or $Ca_{0.8}Sr_{0.2}TiO_3$ inherently has a high sintering temperature (> 1350 °C) and a high loss (< 5000 GHz) [11], which would significantly sacrifice the $Q \times f$ value of the matrix composition for achieving a near-zero τ_f value. By comparison, $Ba_3(VO_4)_2$ (BV) is a superior τ_f compensator due to its large positive τ_f value (~ +52 ppm/°C) and especially good dielectric performances ($\varepsilon_r = 14$ and $Q \times f = 42{,}000$ GHz) as well as relatively low temperatures (~ 1100 °C) [12]. It has been used in many composite ceramics, for instance, BV-$LiMg_{0.9}Zn_{0.1}PO_4$, BV-$BaWO_4$, BV-$Zn_{2-x}SiO_{4-x}$, BV-Mg_2SiO_4, BV-$Li_3(Mg_{0.92}Zn_{0.08})_2NbO_6$ and *etc.* [13–17], in which the sintering temperature could be lowered obviously in addition to satisfactory microwave dielectric properties.

LiF was often used to improve the sintering behavior of Li-based dielectric ceramics and successfully reduced the sintering temperature below 950 °C [18–21]. The 3 wt% LiF aided $Li_2Mg_3SnO_6$ (L_2MS) ceramics were reported to have excellent microwave dielectric properties of $\varepsilon_r = 11.6$, $Q \times f = 133{,}000$ GHz and $\tau_f = -37$ ppm/°C as sintered only at 875 °C [19]. In this study, $(1-x)L_2MS$-xBV-3 wt% LiF (x in volume fraction) ceramics were investigated for the purpose to achieve a desirable LTCC microwave dielectric ceramic with a low loss and a near-zero τ_f, in which LiF played a crucial role in both further reducing the sintering temperature, and suppressing the possible reaction or

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inter-diffusion between L_2MS and BV due to the reduced sintering temperature.

2. Experimental procedure

L_2MS and BV powders were synthesized by means of a conventional mixed-oxide route using high-purity (> 99%) raw powders of Li_2CO_3, MgO, SnO_2, $BaCO_3$, LiF (Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and V_2O_5 (Shandong Xiya Reagent Chemistry Co., Ltd, Linshu, China) according to their respective stoichiometric proportions. Powder mixtures were ball-milled for 8 h in alcohol. After drying, L_2MS and BV powders were calcined at 1100 °C and 800 °C for 8 h, respectively. Afterwards, the pre-calcined powders were weighed according to the prescribed formula of $(1 – x)L_2MS$-xBV (x = 0.20–0.55 in volume fraction) together with 3 wt% LiF as a sintering aid. After being re-milled for 6 h, the fine powders were granulated with 5 wt% PVA as a binder and then subsequently pressed into cylinders with dimensions of 10 mm in diameter and 5–6 mm in height. These samples were sintered in air in the temperature range from 750 °C to 900 °C for 6 h. For the chemical compatibility test, the above-mentioned powder mixture was co-fired with 30 wt% Ag powder at 850 °C for 6 h. To prevent lithium evaporation during sintering, green pellets were buried in the powder of the same composition.

The bulk densities of the sintered ceramics were measured using the Archimedes method. The crystalline phases were identified by an X-ray diffractometer (XRD; D/Max2500 V, Rigaku, Tokyo, Japan). The microstructure of the sintered samples was observed using a field-emission scanning electron microscope (FE-SEM; SU8020, JEOL, Tokyo, Japan) equipped with an energy-dispersive X-ray spectroscope (EDS). Microwave dielectric properties were measured by the Hakki-Coleman method and the $TE_{01\delta}$-shield cavity method with a network analyzer (N5230C; Agilent, Palo Alto, CA) [22] in the frequency range of 9–13 GHz. The τ_f value of the samples was measured in the temperature range from 20 °C to 80 °C.

3. Results and discussion

The normalized XRD patterns of a few powder samples are displayed in Fig. 1. As shown in Fig. 1(a), all diffraction peaks of the as-calcined L_2MS and BV powders could be indexed to the standard patterns of L_2MS (PDF #39-0932) and BV (PDF #29-0211), respectively, indicating that pure L_2MS and BV have been successfully prepared. The former exhibits a cubic rock-salt structure with *Fm*-3*m* space group while the latter belongs to a rhombohedral structure with *R*-3*m* space group. The big difference in their crystal structures would guarantee the coexistence of BV and L_2MS phases in the co-fired sample. As indicated in Fig. 1(b), only L_2MS and BV phases were observed in the $0.63L_2MS$-0.37BV-0.03LiF ceramic sintered at 850 °C and 900 °C, indicating that there is no chemical reaction among BV, L_2MS and LiF. However, when sintering temperature was lower than 850 °C, an additional phase $Li_4MgSn_2O_7$ (L_4MS, PDF #37-1164) appeared in the sample and its concentration slightly increased with decreasing sintering temperature from 775 °C to 750 °C. In order to illustrate the origin of the secondary phase L_4MS, the XRD patterns of L_2MS, L_2MS-0.03LiF and BV-0.03LiF ceramics sintered at 800 °C for 6 h were used for comparison. No any secondary phase can be observed in the BV-0.03LiF sample sintered at 800 °C. Moreover, the same phase composition was observed in both L_2MS and L_2MS-0.03LiF samples as they were sintered at 800 °C. Apart from the dominant phase L_2MS, both samples contained the secondary phase L_4MS. In combination with the XRD result of $0.63L_2MS$-0.37BV-0.03LiF sintered at 850 °C or 900 °C, one can believe that the appeared secondary phase L_4MS should come from the low-temperature decomposition of L_2MS. As manifested by the phase diagram of Li_2SnO_3-MgO [23], L_4MS exists at lower temperatures and tends to transform into the MgO-structured solid solution (*i.e.* L_2MS in this work) as sintering temperature increases above a certain value, which depends on the molar ratio of Li_2SnO_3 and MgO. That is the reason why a slightly increased amount of L_4MS could be observed as sintering temperature was reduced down to 750 °C.

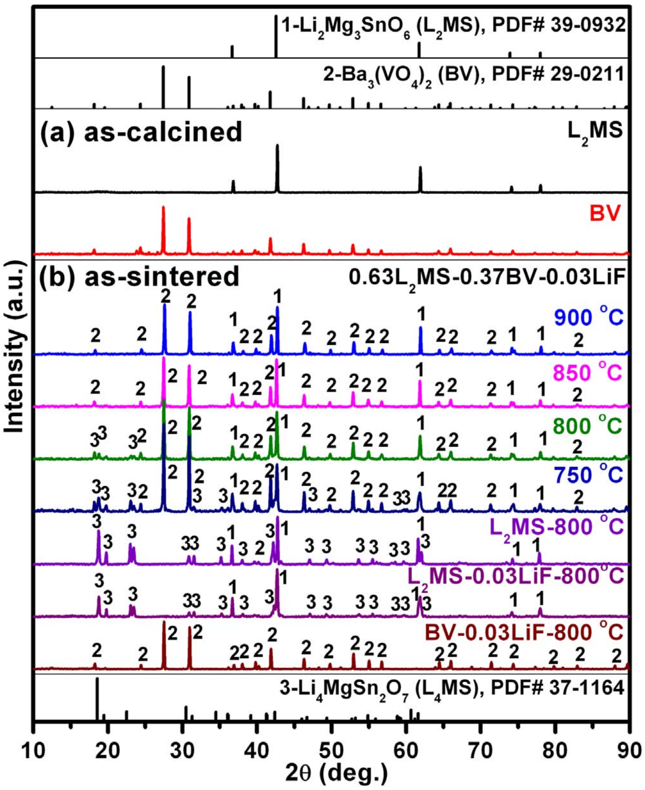

Fig. 1. XRD patterns of (a) BV and L_2MS samples as calcined and (b) different samples sintered at varying temperatures as indicated compared with the standard patterns of L_2MS, BV and L_4MS.

Fig. 2 shows SEM images of the x = 0.37 sample sintered at 850 °C for 6 h. The secondary electron image shown in Fig. 2(a) indicates a dense microstructure with closely packed polygonal grains (~ 2 μm in average). It is almost impossible to distinguish the grains between L_2MS and BV phases from the grain morphology. However, the coexisting two phases can be clearly identified from the corresponding backscattered electron image shown in Fig. 2(b), where there were two kinds of grains with different gray levels owing to the mass difference of the elements in the respective grain. The EDS result listed in Table 1 shows that the dark grains (marked as spectrum 1 in Fig. 2(b)) mainly contained Mg, Sn, O elements with an approximate molar ratio of Mg:Sn:O = 3:1:6 (lithium is too light to be precisely detected by EDS), which approximately corresponds to the composition of L_2MS. The light grains (marked as spectrum 2 in Fig. 2(b)) were dominantly composed of Ba, V, and O elements with a Ba:V ratio of ~ 3:2, suggesting that these grains belong to the BV phase. The above analysis further illustrates a composite structure of the x = 0.37 sample consisting of L_2MS and BV phases, which agreed well with the XRD results in Fig. 1. In addition, it can be also seen from Table 1 that a few amount of Ba^{2+} and V^{5+} were detected in the L_2MS grain, meanwhile some Mg^{2+} and Sn^{4+} appeared in the BV grain, indicating the existence of the ionic inter-diffusion between the two phases during co-sintering. The similar phenomena were also observed in the BV–$LiMg_{0.9}Zn_{0.1}PO_4$ and BV-$Li_3(Mg_{0.92}Zn_{0.08})_2NbO_6$ composite ceramics [13,17].

Relative density and microwave dielectric properties of (1 − x) L_2MS-xBV-0.03LiF ceramics sintered at different temperatures are shown in Fig. 3. With increasing sintering temperature, the relative density of all specimens increased to the maximum values approximately at 775 °C, and then remained almost constant (> 95%) within the studied temperature range (≤ 900 °C). This result indicates that the

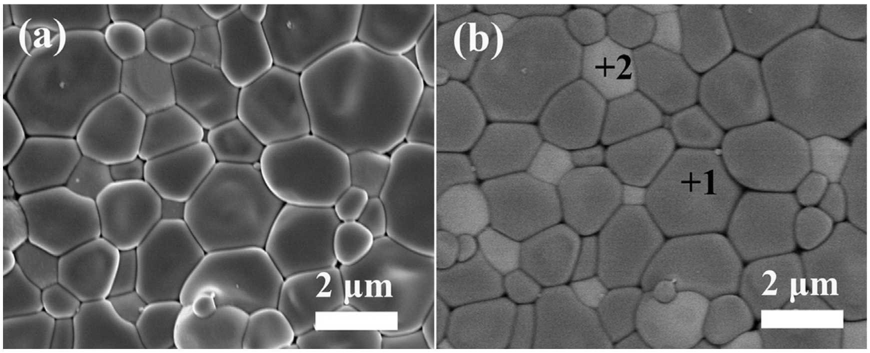

Fig. 2. (a) Secondary electron image and (b) backscattered electron image on the polished and thermally etched surface of the x = 0.37 sample sintered at 850 °C for 6 h.

Table 1
EDS results of the x = 0.37 sample as shown in Fig. 2(b).

Points	Elements (at%)					Total (%)
	Mg	Sn	Ba	V	O	
1	29.5	12.1	0.8	0.4	57.2	100.0
2	10.1	3.6	30.1	18.2	38.0	100.0

addition of 3 wt% LiF effectively promoted the densification of (1 − x) L_2MS-xBV ceramics and made them well densified within a relatively low sintering temperature [19]. The variation of ε_r and $Q \times f$ values with sintering temperature showed a similar trend to that of the relative density, indicating that both ε_r and $Q \times f$ values mainly depended on the sample density in this work. The secondary phase formed below 850 °C did not bring obvious effects on the dielectric properties of the matrix, implying that L_4MS probably owns a similar dielectric performance with L_2MS. As the sintering temperature was higher than 775 °C, ε_r and $Q \times f$ generally kept nearly constant for samples with a certain x value. However, for samples with different x values, their dielectric properties were found to be strongly dependent on the relative content of L_2MS and BV, as shown in Fig. 3(d). Fig. 3(d) indicates that ln ε_r, $(Q \times f)^{-1}$, and τ_f values displayed a nearly linear variation as a function of x, which is in good agreement with a well-known empirical model for multiphase ceramics described as follows [24,25]:

$$\ln \varepsilon_r = V_1 \ln \varepsilon_{r1} + V_2 \ln \varepsilon_{r2} \quad (1)$$

$$(Q \times f)^{-1} = V_1 (Q \times f)_1^{-1} + V_2 (Q \times f)_2^{-1} \quad (2)$$

$$\tau_f = V_1 \tau_{f1} + V_2 \tau_{f2} \quad (3)$$

where V_1 and V_2 stand for the volume fraction of each phase. A slight deviation between the experimental and calculated ln ε_r and $(Q \times f)^{-1}$ values could be clearly observed, as also found in other studies [15,25]. One reason might be ascribed to the fact that the distribution of two phases is not perfectly uniform in the sintered ceramic body. Moreover, the microwave dielectric properties of these two phases in the

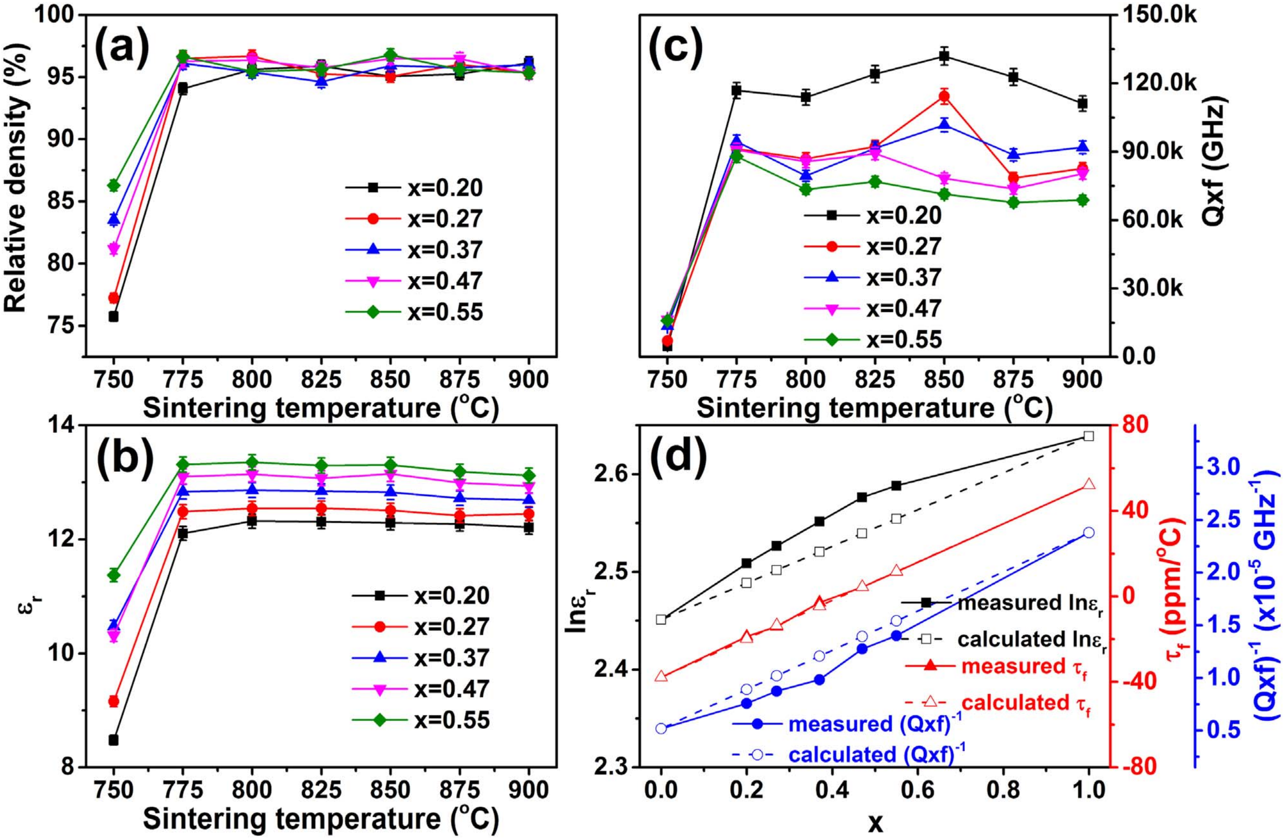

Fig. 3. (a) Relative density, (b) ε_r and (c) $Q \times f$ values of (1 − x)L_2MS-xBV-0.03LiF ceramics sintered at different temperatures, and (d) the measured and calculated dielectric properties with changing the volume fraction (x) of BV for samples sintered at 850 °C for 6 h.

Table 2
A comparison of microwave dielectric properties among a few LTCC ceramics with rock salt structure.

Compounds	S.T. (°C)	ε_r	$Q \times f$(GHz)	τ_f (ppm/°C)	*Ref.*
$0.8Li_2Mg_3TiO_6$-$0.2Ca_{0.8}Sr_{0.2}TiO_3$ -4 wt% LiF	800	18.8	48,200	0.3	[8]
$0.7Li_3(Mg_{0.92}Zn_{0.08})_2NbO_6$–0.3BV	950	16.3	50,084	1.5	[17]
Li_2MgTiO_4-10 wt%LiF -12 wt% $Ca_{0.8}Sr_{0.2}TiO_3$	900	18	34,800	4	[20]
Li_2SnO_3-8 wt% MgO-2 wt% LiF	880	14.7	78,400	−0.9	[21]
$0.63L_2MS$-0.37BV-0.03LiF	850	12.8	101,705	−2.9	This work

S.T.: sintering temperature; *Ref.*: references.

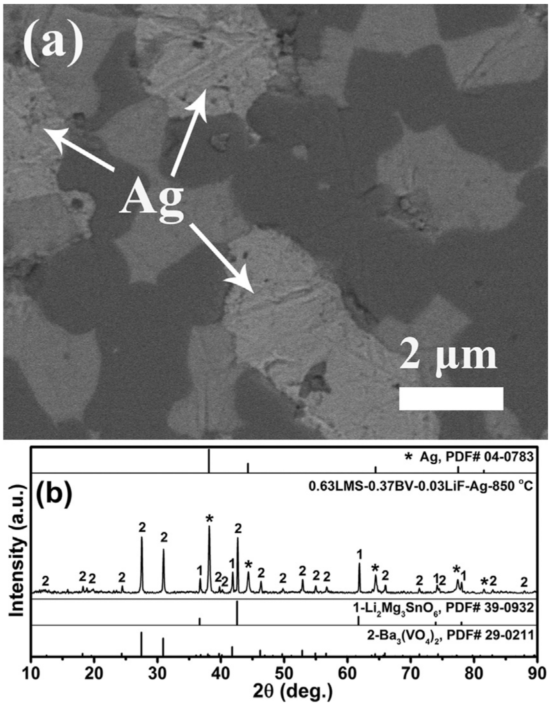

Fig. 4. (a) Backscattered electron image and (b) XRD pattern of the x = 0.37 sample co-fired with Ag at 850 °C for 6 h.

composite ceramic might be different from those in their respective monophasic ceramics owing to the ionic inter-diffusion during sintering [26], as discussed above. By contrast, a nearly linear curve was observed for both experimental and calculated τ_f values with increasing x, apart from their close values. This may be due to the fact τ_f is more sensitive to the intrinsic structure of each phase, which was nearly unchanged before and after sintering. Nevertheless, excellent microwave dielectric properties of ε_r = 12.8, $Q \times f$ = 101,705 GHz (@ 9.64 GHz) and τ_f = −2.9 ppm/°C were achieved in the x = 0.37 ceramic sintered at 850 °C for 6 h. A comparison of microwave dielectric properties for a few LTCC ceramics with similar structures was made, as shown in Table 2. Among these ceramics, it is easy to find that high $Q\times f$ values and low sintering temperatures in current $0.63L_2MS$-0.37BV-0.03LiF composite ceramic made it have relatively large potentials against others.

For the chemical compatibility test, the composite ceramic powder was co-fired with 30 wt% Ag powder at 850 °C for 6 h. As shown in Fig. 4(a), the backscattered electron image clearly indicated that silver particles can stably exist in the $0.63L_2MS$-0.37BV-0.03LiF ceramic after sintering. A clear interface between the ceramic particles and silver particles suggested no chemical reaction between them. This can be further confirmed by the corresponding XRD result shown in Fig. 4(b). All diffraction peaks of the co-fired sample can be well indexed to the L_2MS, BV, and Ag. As a result, the composite ceramic reported in current study possesses a good chemical compatibility with Ag electrodes in addition to excellent microwave dielectric properties, being expected as a promising candidate material for LTCC applications.

4. Conclusions

The phase composition, microstructure and microwave dielectric properties of the (1 − x)L_2MS-xBV-0.03LiF composite ceramics were systematically investigated, in which LiF and BV acted as a sintering aid and a τ_f compensator, respectively. The XRD results reveal that L_2MS and BV phases stably coexisted in the sintered ceramics at the sintering temperature up to at least 900 °C. At temperatures lower than 800 °C, the appearance of a secondary phase L_4MS stemmed from the low-temperature decomposition of L_2MS, irrespective of the existence of BV and LiF, through which a low-temperature sintering and a near-zero τ_f can be obtained by adjusting the relative content of BV and L_2MS according to a well-known mixing rule. Excellent microwave dielectric properties of ε_r = 12.8, $Q \times f$ = 101,705 GHz (@ 9.64 GHz) and τ_f = −2.9 ppm/°C were achieved in the x = 0.37 sample sintered at 850 °C for 6 h. Furthermore, the $0.63L_2MS$-0.37BV-0.03LiF composite ceramic has a good chemical compatibility with Ag, suggesting its great potential for LTCC applications.

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