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Sintering Characteristics and Microwave Dielectric Properties of $Li_2Mg_3Ti_{0.95}(Mg_{1/3}Sb_{2/3})_{0.05}O_6$ Ceramic Doped with LiF for LTCC Applications

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In the current study, LiF as a sintering agent was chosen to achieve the low temperature sintering of $Li_2Mg_3Ti_{0.95}(Mg_{1/3}Sb_{2/3})_{0.05}O_6$ (LMTS) ceramics. LMTS ceramics with 1–4 wt.% LiF additions were prepared by a solid-state reaction. The influence of LiF-doping on x-ray diffraction patterns, apparent density, micro-morphology and microwave dielectric properties were discussed in depth. With different LiF additions, LMTS ceramics show a rock salt structured pure phase. A small amount of LiF addition can significantly promote sintering due to the liquid-phase sintering. Compact samples (> 95% of theoretical density) can be obtained at 950°C for LMTS with 2–4 wt.% LiF addition ceramics. Particularly, LMTS with 4 wt.% LiF additional ceramic exhibited optimal microwave dielectric properties at 950°C ($\varepsilon_r = 14.9$, $Q \times f = 68132$ GHz and $\tau_f = -39.24$ ppm/°C). Moreover, LMTS ceramics possessed excellent chemical compatibility with silver, implying that the LMTS-LiF ceramic is a potential candidate for low temperature co-fired ceramic (LTCC).

Key words: $Li_2Mg_3Ti_{0.95}(Mg_{1/3}Sb_{2/3})_{0.05}O_6$, LiF, microwave dielectric ceramics, LTCC

INTRODUCTION

As for the development of wireless communication systems, there is a higher demand for microwave dielectric materials. Low temperature co-fired ceramic (LTCC) has exerted enormous interest as a result of the multilayer structure which can accelerate the progress of miniaturization and integration technologies in microwave devices.[1–3] Usually, microwave dielectric ceramics met the requirements: a suitable dielectric constant (ε_r), a higher quality factor ($Q \times f > 1000$ GHz) and a near-zero temperature coefficient of resonant frequency (τ_f).[3] And till now several ceramics were reported, such as $CoZrTa_2O_4$,[4] Na_2O-Nd_2O_3-CeO_2,[5] $NiZrNb_2O_8$,[6] $ZnTa_2O_6$,[7,8] possessing great microwave dielectric properties. Moreover, the sintering temperature is required to be lower than the melting point of silver (~ 961°C) for LTCC applications. However, the sintering temperatures of these materials are usually too high for LTCC technology. Therefore, it is essential to explore materials sintered below 950°C possessing suitable microwave dielectric properties by using the sintering additives such as CuO, LiF or other aids.[9–12]

Recently, $Li_2Mg_3TiO_6$-based ceramics with exhibit excellent microwave dielectric properties were reported as shown in Table I.[13–23] Fu et al. reported that the $Li_2Mg_3TiO_6$ ceramic showed good properties at 1280°C ($\varepsilon_r \sim 15.2$, $Q \times f \sim 152{,}000$ GHz and $\tau_f \sim -39$ ppm/°C).[13] The effects of substitution of equivalent cations for Mg^{2+} ions on microwave properties were studied by Zhang et al., and the $Li_2(Mg_{0.95}Zn_{0.05})_3TiO_6$ ceramic was prepared with properties of $\varepsilon_r = 14.6$, $Q \times f = 158{,}000$ GHz, $\tau_f = 3.2$ ppm/°C at 1275°C for 6 h.[16] The temperature-stable $Li_2Mg_{2.88}Ca_{0.12}TiO_6$ ceramic was synthesized by Fang et al.[17] Fu et al. successfully prepared

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Table I. Microwave dielectric properties of $Li_2Mg_3TiO_6$-based microwave dielectric ceramics

Formula	S.T. (°C)	ε_r	$Q \times f$ (10^4 GHz)	τ_f
$Li_2Mg_3TiO_6$[13]	1280	15.2	15.2	– 39
$Li_2Mg_3TiO_6$[14]	1360	14.4	15.3	– 11.1
$Li_2Mg_3TiO_6$[15]	1275	13.6	11.7	– 35.1
$Li_2(Mg_{0.95}Zn_{0.05})_3TiO_6$[16]	1275	14.6	15.8	3.2
$Li_2Mg_{2.88}Ca_{0.12}TiO_6$[17]	1280	17.8	10.2	– 0.7
$Li_2Mg_3TiO_6$-4 wt.% LiF[18]	950	16.2	13.1	– 44
$Li_2Mg_3TiO_6$-2 wt.%LiF-2 wt.% CuO[19]	950	15.7	7.0	– 43
$0.9Li_2Mg_3TiO_6$-$0.1SrTiO_3$-4 wt.% LiF[20]	900	19.5	6.4	6.5
$0.8Li_2Mg_3TiO_6$-$0.2Ca_{0.8}Sr_{0.2}TiO_3$-4 wt.%LiF[21]	800	18.8	4.8	0.3
$Li_2(Mg_{1-x}Co_x)_3TiO_6$[22]	1600	14.2	10.1	– 12.4
$Li_2Mg_3Ti_{0.95}(Mg_{1/3}Sb_{2/3})_{0.05}O_6$[23]	1575	14.4	19.6	– 4.02
$Li_2Mg_3Ti_{0.95}(Mg_{1/3}Sb_{2/3})_{0.05}O_6$-4 wt.% LiF	950	14.9	6.8	– 39.2

S.T. means sintering temperature.

$Li_2Mg_3TiO_6$-4wt.% LiF ceramics at 950°C with excellent properties: ε_r = 16.2, $Q \times f$ = 131,000 GHz, τ_f = – 44 ppm/°C.[18] In our previous works, crystal structure, intrinsic factors and microwave dielectric properties of $Li_2Mg_3Ti_{0.95}(Mg_{1/3}Sb_{2/3})_{0.05}O_6$ (LMTS) were investigated, and the properties of $\varepsilon_r \sim 14.395$, $Q \times f \sim 196{,}000$ GHZ, $\tau_f \sim$ 4.016 ppm/°C were gained at 1575°C for 4 h.[23] However, there has been little research on LMTS ceramic for LTCC applications until now. Besides, it has been reported that LiF addition can efficiently reduce the densification sintering temperature of ceramics, owing to liquid-phase sintering.[24,25] In this paper, LMTS-*x* wt.% LiF ceramics were prepared and the phase composition, sintering behavior, micro-morphology and microwave dielectric properties were systematically investigated.

EXPERIMENTAL

LiF doped LMTS ceramics were prepared by traditional solid-state reaction. Li_2CO_3 (99.99%), Sb_2O_5 (99.95%), MgO (99.99%), TiO_2 (99.80%) powders were weighted according to stoichiometric ratio and mixed with ethanol medium in a nylon jar for 12 h. The mixtures were dried and calcined at 80°C and 1000°C, respectively. Then powders were remilled with *x* wt.% LiF (99%) (x = 1, 2, 3 and 4) for 12 h. After drying again, mixtures mixed with 8 wt.% paraffin were pressed into pellets that were 10 mm in diameter and 6 mm in height. All specimens were heated at 500°C for 4 h to expel the binder. Finally, LMTS ceramics doped with various content of LiF were sintered at 850–1050°C for 4 h.

The phase composition was identified using x-ray diffraction (XRD) with Cu$K\alpha$ radiation. The apparent density was tested by the Archimedes method. The microstructure was analyzed by a scanning electron microscope (SEM) (Model JEOL JEM-2010, FEI Co., Japan). The microwave dielectric properties were obtained using a network analyzer (N5234A, Agilent Co., USA). The relative permittivity was measured by Hakki–Coleman.[26] The cavity method was used to measure unloaded quality factors.[27] The value of τ_f was calculated by Eq. 1,

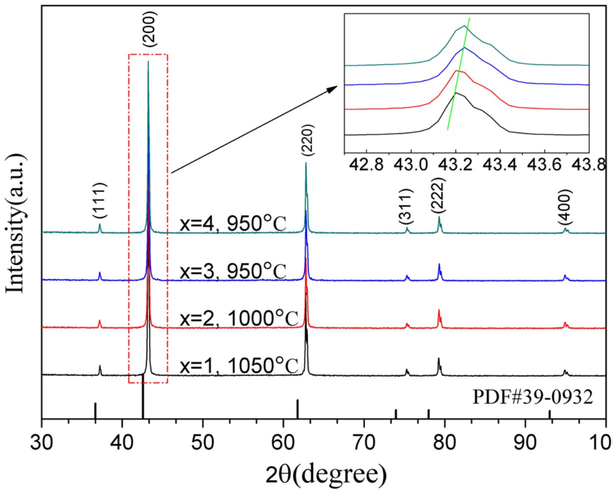

Fig. 1. XRD patterns of LMTS-*x* wt.% LiF ceramics sintered at optimum temperatures for 4 h and the variation of (200) diffraction peaks as a representative shown in the inset.

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

where the f_1 and f_2 were resonance frequencies at the temperatures of T_1 (25°C) and T_2 (85°C), respectively.

RESULTS AND DISCUSSION

Figure 1 exhibits XRD patterns of different LiF doped LMTS ceramics sintered at the optimum temperature. All diffraction peaks were indexed to the $Li_2Mg_3SnO_6$ phase (JCPDS No. 39-0932), also a rock salt structure belonging to Fm-3m (225) space group was detected. Besides, all samples exhibited a pure single phase without a second phase observed. As shown in the insert, the diffraction peak (200) shifted to the higher angle with the increase of LiF content. This phenomenon could be connected with the F^- ion (R = 1.33 Å) substituting for larger O^{2-} (R = 1.4 Å) ion, which caused the cell volume reduction. Analogous results have been reported by Liu et al.[18]

Figure 2 shows the apparent densities of LMTS-x wt.% LiF ($1 \le x \le 4$) ceramics sintered at various temperatures. The lower density was gained at the sintering temperature region of 850–1050°C for LMTS-1 wt.% LiF ceramics, which indicated that it is difficult to effectively reduce the sintering temperatures when x = 1. In the case of $x \ge 2$, the densities increased as the increase of temperature due to the sintering process, and then showed a slightly lessened trend which could be attributed to abnormal grain growth at higher temperatures. And pores are an important factor to affect dielectric constant because of their low relative permittivity (ε = 1). The optimum density (about 3.39 g/cm^3) for LMTS-2 wt.% LiF ceramic was gained at the sintering temperature of 900°C. This value was similar to maximum density (about 3.38 g/cm^3) of LMTS ceramics at 1575°C.[23] The maximum density of LMTS-x wt.% LiF (x = 2, 3 and 4) samples showed no obvious change of 3.37–3.39 g/cm^3. As a result, a certain amount of LiF addition could effectively facilitate densification and reduce the sintering temperature.

Figure 3 illustrats the SEM micrographs of LMTS doped with various amounts of LiF ($1 \le x \le 4$) ceramics sintered at optimal temperature. As exhibited in Fig. 3a, larger grain and numerous pores were observed for samples with 1 wt.% LiF addition sintered at 1050°C, which might degenerate

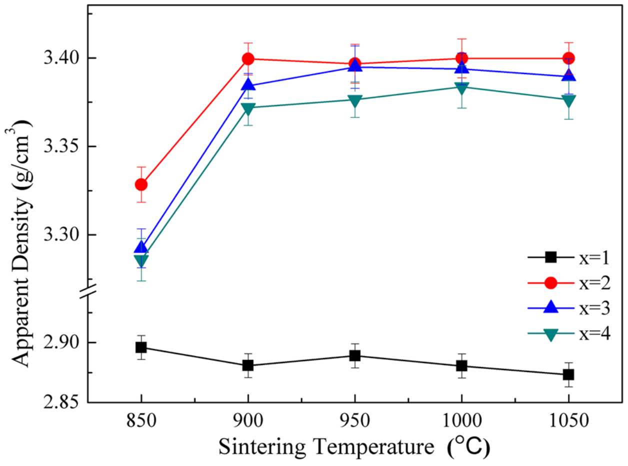

Fig. 2. Apparent density of LMTS-x wt.% LiF ceramics sintered at different temperatures.

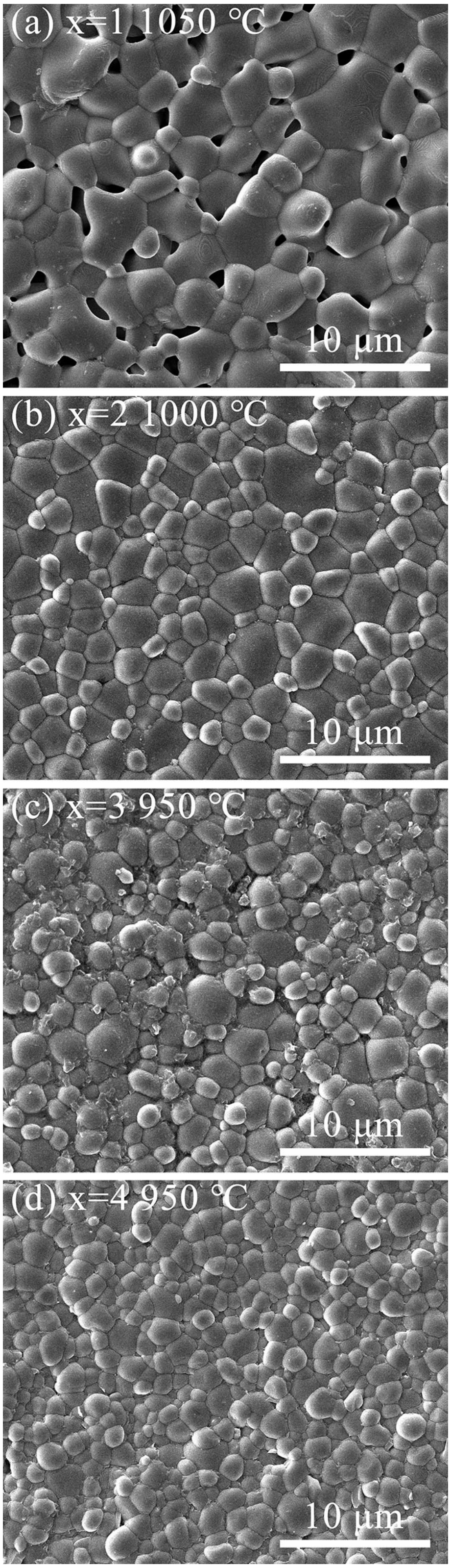

Fig. 3. SEM images of LMTS-x wt.% LiF ceramics sintered at optimum temperatures. [(a) x = 1 at 1050°C, (b) x = 2 at 1000°C, (c) x = 3 at 950°C, (d) x = 4 at 950°C].

dielectric properties. A series of dense microstructures were gained at the optimal sintering temperature of 1000°C, 950°C and 950°C for LMTS doped with 2, 3, and 4 wt.% LiF ceramics, respectively, as a result of accelerating boundary diffusion coefficients attributed to the liquid-phase sintering.[21] Among them, LMTS-4 wt.% LiF ceramic possessed dense microstructure and uniform grain size of 1.94 μm at 950°C as shown in Fig. 3d, which might result in excellent microwave dielectric properties and indicate that LiF doping can effectively facilitate the densification.

Figure 4 demonstrates the dielectric constant for LMTS ceramics with various amounts of LiF addition sintered at different temperatures. It was reported that densification, dielectric polarizability and crystal structure are related to the dielectric constant.[28,29] For LMTS-x wt.% LiF $(2 \le x \le 4)$ ceramics, the dielectric constants increased firstly, reaching maximum values about 15 at the sintering temperature of 900–950°C and then showed a small decreasing trend with further increasing temperature. For LMTS ceramics with 1 wt.% LiF addition samples, a series of lower ε_r values about 11.7 were observed at different temperatures. The variation of relative permittivity exhibited a similar tendency with the density as the sintering temperature increased. The increase of ε_r might be mainly due to gain growth and pores being eliminated, and the decrease of ε_r could be related to abnormal grain growth. In addition, the lower ε_r values for LMTS-1 wt.% LiF ceramics might be related to the porous microstructure shown in Fig. 3a. Therefore, the densification was an important factor to affect the dielectric constant in this work.

The relationship between quality factor and sintering temperature of LMTS-x wt.% LiF $(1 \le x \le 4)$ is demonstrated in Fig. 5. The $Q \times f$ was usually governed by extrinsic and intrinsic factors.[30–33] Intrinsic factors possessed crystal structure, packing fraction and bonding characteristics,[30,31] while extrinsic factors include compactness, grain sizes, second phase and oxygen vacancies.[32,33] In this work, the variation of quality factor was different from that of density and ε_r. As the sintering temperature increased, the $Q \times f$ values increased first and then exhibited a decreasing tendency. The maximum $Q \times f$ values were gained at 1050°C, 1000°C, 950°C and 950°C for LMTS-x wt.% LiF ceramics (x = 1, 2, 3, 4), respectively. As mentioned above, the maximum ε_r values for LMTS doped with 2–4 wt.% LiF were gained at 900°C, which were lower than the optimum sintering temperature of $Q \times f$ for different LiF doped LMTS ceramics. The increased value of the quality factor might be related to the increase of grain size, whereas the decrease might owe to an abnormal grain growth as further increasing of sintering temperature. The lower values of $Q \times f$ for LMTS-1 wt.% LiF ceramics might depend on the porous

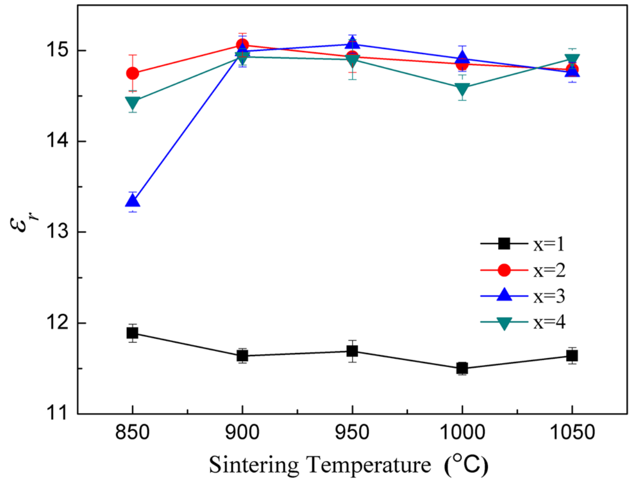

Fig. 4. Variation of dielectric constant for LMTS-x wt.% LiF ceramic with different sintering temperatures.

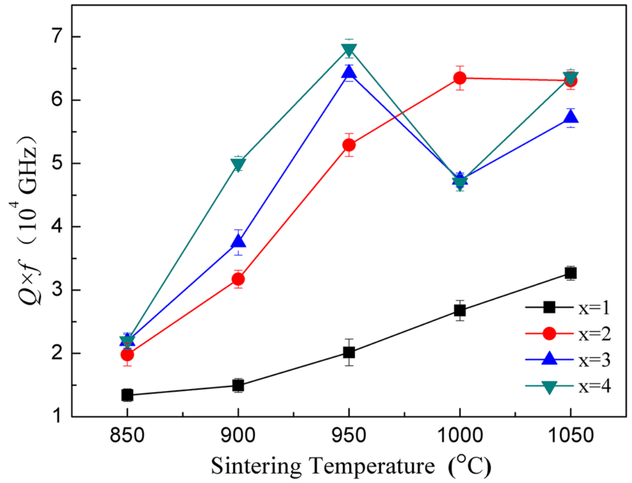

Fig. 5. $Q \times f$ values of LMTS-x wt.% LiF ceramics sintered at different temperatures.

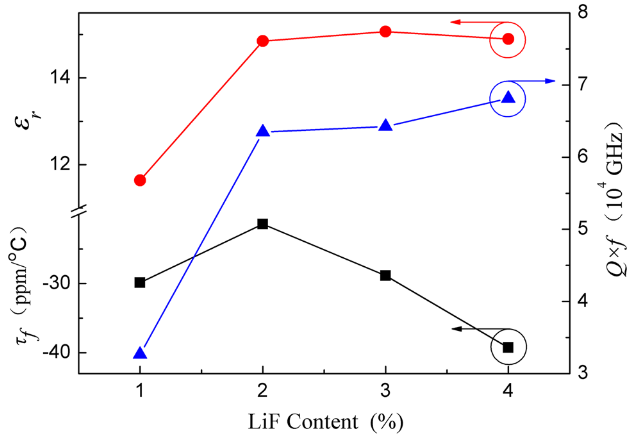

Fig. 6. Microwave dielectric properties of LMTS-x wt.% LiF ceramics sintered at optimum temperatures.

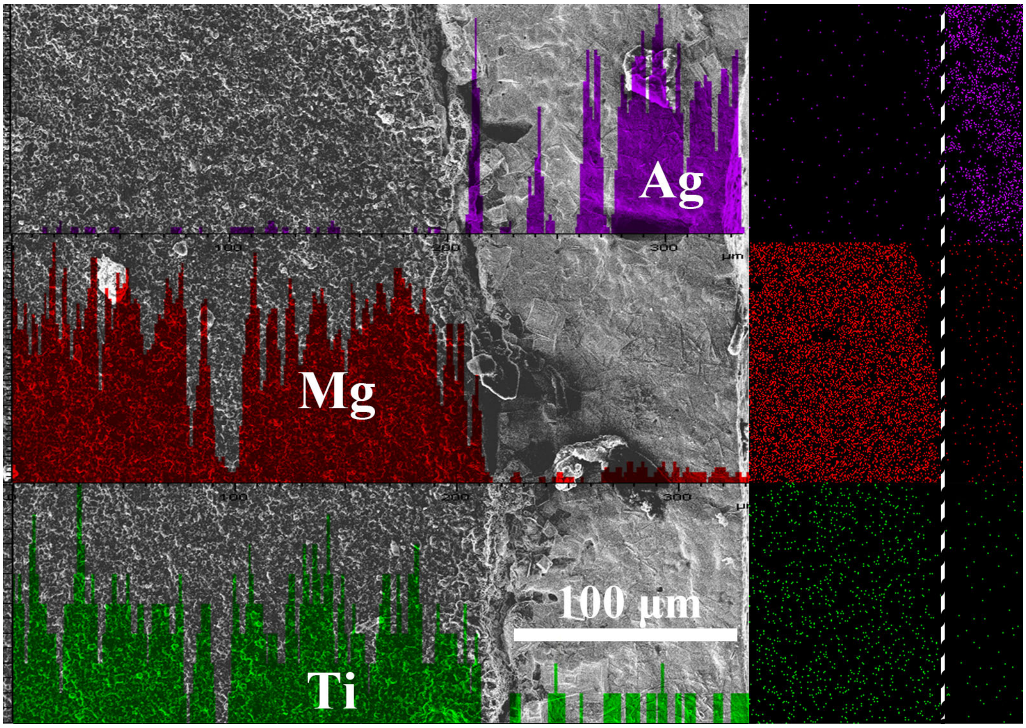

Fig. 7. Fracture surface SEM and EDS analysis of the LMTS-4 wt.% LiF ceramic co-fired with Ag at 950°C.

microstructure in Fig. 3a. The optimum quality factor of 68,132 GHz was obtained for LMTS ceramic doped 4wt.% LiF at 950°C.

The variations of ε_r, $Q \times f$ and τ_f values with LiF addition for LMTS-x wt.% LiF ceramic ($1 \le x \le 4$) at optimum sintering temperature are presented in Fig. 6. The value of ε_r increased first and reached a maximum value at $x = 2$, then did not have an obvious change with further increasing LiF content, which exhibited a similar tendency to density. The variation of quality factor values was similar to that of ε_r as the increase of LiF addition, a higher value of $Q \times f$ was successfully gained at lower sintering temperature of 950°C for LMTS-4 wt.% ceramic, and this value did not decrease compared to LMTS-2 wt.% LiF ceramic sintered at 1000°C. Besides, in the case of ceramics being dense (x = 2, 3 and 4), the value of τ_f decreased from − 21.41 ppm/°C to − 39.24 ppm/°C with the LiF content increasing, which might be attributed to the glass phase existing. As a result, LMTS doped with 4wt.% LiF ceramic exhibited excellent microwave dielectric properties ($\varepsilon_r = 14.9$, $Q \times f$ = 68,132 GHz, τ_f = − 39.24 ppm/°C at 950°C).

For purpose of investigating the chemical compatibility of LMTS ceramics with silver, 4 wt.% LiF doped LMTS ceramic was co-fired with Ag electrode at 950°C. The fracture surface SEM micrograph with EDS line scanning and surface scanning analysis were exhibited in Fig. 7. A clear boundary marked as dotted line was obtained for surface scanning, while the similar result was obtained in line scanning. It was proved that there were no reactions between 4wt.% LiF doped LMTS ceramic and Ag electrode at 950°C. As a result, the LMTS-4 wt.% LiF ceramic is a promising candidate for LTCC applications due to well compatibility with silver electrode as well as excellent properties.

CONCLUSIONS

In this work, the rock-salt structure LMTS doped with various amounts of LiF ceramics were successfully prepared. The phase composition, sintering behavior, micro-morphology and microwave dielectric properties for LMTS-x wt.% LiF ceramic ($1 \le x \le 4$) were investigated. Dense samples could be gained at 900–1050°C for LMTS ceramic doped with 2–4 wt.% LiF, indicating that LiF addition could effectively lower sintering temperature and facilitate densification. The ε_r showed the similar tendency as the density. The densification and microstructure were important factors to affect microwave dielectric properties. Particularly, for LMTS doped with 4 wt.% LiF ceramics, excellent microwave dielectric properties ($\varepsilon_r = 14.9$, $Q \times f$ = 68,132 GHz, τ_f = − 39.24 ppm/°C) were gained at 950°C. Moreover, LMTS ceramics possessed excellent chemical compatibility with silver, which met the requirement of LTCC.

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