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Low temperature sintering and microwave dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ ceramics for LTCC applications

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Abstract

The effects of $MnCO_3$–CuO and Li_2O–B_2O_3–SiO_2 (for short LBS) on the sintering behavior, microstructures and microwave dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ ceramics have been investigated. The pure $Ba_2Ti_3Nb_4O_{18}$ ceramics sintered at 1220 °C showed microwave dielectric properties: $\varepsilon_r = 38$, $Q \times f = 23{,}700$ GHz (at 4.8 GHz), and $\tau_f = -3$ ppm/°C. It was found that a small amount of $MnCO_3$–CuO and LBS glass additives lowered the sintering temperature of $Ba_2Ti_3Nb_4O_{18}$ ceramics effectively from 1220 °C to 900 °C. The dielectric constant (ε_r) increased and the temperature coefficient of the resonant frequency shifted to a positive value with the addition of $MnCO_3$–CuO and LBS, which were mainly due to the presence of the second phase $Ba_3Ti_4Nb_4O_{21}$. $Ba_2Ti_3Nb_4O_{18}$ ceramics with 1.5 wt% $MnCO_3$–CuO and 0.5 wt% LBS sintered at 900 °C for 2 h showed dielectric properties: $\varepsilon_r = 41$, $Q \times f = 15{,}000$ GHz (at 4.8 GHz), and $\tau_f = 4$ ppm/°C. It was compatible with Ag electrodes, which made it a promising ceramic for low temperature co-fired ceramics technology application.

Keywords: Dielectric properties; Sintering; LTCC; $Ba_2Ti_3Nb_4O_{18}$

1. Introduction

With the recent progress of advanced communication systems, including mobile and satellite communications, multi-layer microwave devices have been widely used in microwave circuits to miniaturize related components.[1] The development of low temperature co-fired ceramics (LTCC) technology for microwave applications has received much attention, because of the design and functional benefits upon the miniaturization of multi-layer devices with high electrical performance by using highly conductive internal electrode metals, such as silver and copper.[2] Several approaches have been reported to reduce the sintering temperature of dielectric materials including the low-melting glass addition or oxides, chemical processing and nanosized powders. Among these methods, low-melting glass additions and oxides for liquid-phase sintering are lower in cost and easier to process than the others. Low temperature sintering of dielectric materials with glass frits or oxides have been successfully achieved by several microwave dielectric ceramics systems such as $BiNbO_4$, CaO–SiO_2, ZnO–SiO_2, MgO–TiO_2, ZnO–TiO_2, Li_2O–Nb_2O_5–TiO_2, CaO–Li_2O–Nb_2O_5–TiO_2, BaO–TiO_2, BaO–Ln_2O_3–TiO_2 (Ln = La, Nd, Sm), and $CaWO_4$.[3–12]

The microwave dielectric properties of several ceramics in the BaO–TiO_2–Nb_2O_5 system such as $BaTi_3Nb_4O_{17}$, $Ba_6Ti_{14}Nb_2O_{39}$, $Ba_3Ti_5Nb_6O_{28}$ and $Ba_3Ti_4Nb_4O_{21}$ have been reported.[13,14] Dielectric materials in the BaO–TiO_2–Nb_2O_5 system such as $Ba_3Ti_5Nb_6O_{28}$ ($\varepsilon_r = 41$, $Q \times f = 4500$ GHz, and $\tau_f = 8$ ppm/°C) and $Ba_3Ti_4Nb_4O_{21}$ ($\varepsilon_r = 55$, $Q \times f = 9000$ GHz, and $\tau_f = 100$ ppm/°C)[13]are adequate for practical applications. In general, the sintering temperatures of these ceramics or related compounds are around 1300 °C. Ko et al. and Kim et al. reported that $Ba_3Ti_{4-x}Zr_xNb_4O_{21}$ ($x = 1$) and $Ba_3Ti_5Nb_6O_{28}$ could be densified below 900 °C with glass frits, respectively, but the $Q \times f$ values decreased seriously.[15,16] To our knowledge, the dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ have not been reported and then it is worthwhile to determine whether this material might have equivalent or superior properties. In order to develop $Ba_2Ti_3Nb_4O_{18}$ as a candidate material for multi-layer devices, it is necessary to reduce the sintering temperature of the ceramic available to the co-firing with Ag. In this paper, we report the synthesis, characterization and dielectric properties of

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$Ba_2Ti_3Nb_4O_{18}$ and also make the efforts on studying the effect of $MnCO_3$–CuO and LBS glass additives on the densification and microwave dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ ceramics. Moreover, the compatibility of $Ba_2Ti_3Nb_4O_{18}$ ceramics with Ag electrode is investigated.

2. Experimental procedure

$Ba_2Ti_3Nb_4O_{18}$ were prepared by the conventional solid-state reaction method. The stoichiometric mixtures of powders $BaCO_3$ (≥99%), Nb_2O_5 (≥99%), and TiO_2 (≥98%) were weighed and milled in ethylalcohol medium for 24 h using zirconia balls. The wet powders were dried and calcined in air at 1100 °C for 4 h. For $MnCO_3$–CuO (for short MC), $MnCO_3$ and CuO (≥99%) were weighed according to the compositions of 0.2 $MnCO_3$–0.8 CuO and calcined at 750 °C for 3 h. The $Ba_2Ti_3Nb_4O_{18}$ powders were remilled with MC and home-made Li_2O–B_2O_3–SiO_2 (for short LBS) additives for 24 h. The dried powders were mixed 5% PVA solution and subsequently uniaxially pressed into cylindrical pellets of 18 mm in diameter and 7–9 mm in thickness under a pressure of 80 MPa. The samples were sintered at different temperatures for 2 h with 5 °C/min heating and cooling rate.

The density of the ceramics was measured by the Archimedes method. The crystalline structure of the sintered samples was examined by X-ray powder diffraction using Cu Kα radiation (XRD Rigaku, D/max-RA). The microstructures of specimens were observed by scanning electron microscopy (SEM, FEI SIRION-100) and the compositions were analyzed by energy-dispersive spectroscopy (EDS, EDAX GENENIS-4000). The microwave dielectric properties were measured by the Hakki–Coleman dielectric resonator method, using a network analyzer (Agilent 8719 Et, 0.05–13.5 GHz). The temperature coefficient of the resonant frequency (τ_f) was also measured by the same method by changing temperature from 25 °C to 80 °C and calculated from the equation:

$$\tau_f = \frac{f_{80} - f_{25}}{f_{25} \times 55} \times 10^6 \,(\text{ppm/°C})$$

where f_{80} and f_{25} represent the resonant frequency at 80 °C and 25 °C, respectively.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $Ba_2Ti_3Nb_4O_{18}$ samples sintered at different temperatures for 2 h without any additive. The XRD pattern of $Ba_2Ti_3Nb_4O_{18}$ sintered at 1220 °C for 2 h was fully indexed using the space group $P2_1/c$ with lattice parameters $a = 10.000$ Å, $b = 9.955$ Å, $c = 7.311$ Å, $\beta = 111.19°$, and was in good agreement with JCPDS file No. 77–1205. The crystallography of $Ba_2Ti_3Nb_4O_{18}$ has been reported as monoclinic and had a framework of (Nb, Ti)–O octahedral units.[17] It was found that the crystal structure of samples did not change with increasing temperature, however the intensities of some peaks enhanced with the sample sintered at 1310 °C for 2 h. This was attributed to the size of grains changing as confirmed in Fig. 2. Fig. 2 shows the SEM micrographs of the surfaces of

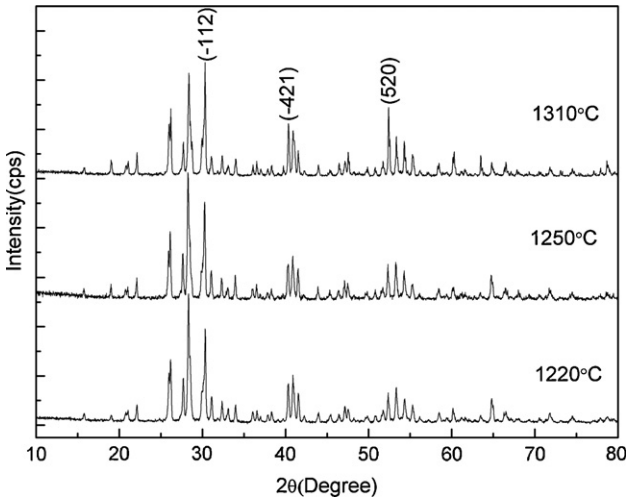

Fig. 1. XRD patterns of $Ba_2Ti_3Nb_4O_{18}$ ceramics sintered at different temperatures for 2 h.

$Ba_2Ti_3Nb_4O_{18}$ sintered at different temperatures for 2 h without any additive. The samples sintered at 1220 °C and 1250 °C showed a dense microstructure without porosity, and the packed grains were in the size range of 2–4 μm. In contrast, abnormal grain growth of $Ba_2Ti_3Nb_4O_{18}$ ceramics was observed with the sample sintered at 1310 °C for 2 h which indicated the sintering temperature (1310 °C) was too high for $Ba_2Ti_3Nb_4O_{18}$ ceramics.

Table 1 represents the bulk density and microwave dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ without additives sintered at 1190–1310 °C for 2 h. It was observed that $Ba_2Ti_3Nb_4O_{18}$ ceramic sintered at 1220 °C for 2 h showed excellent microwave dielectric properties: $\varepsilon_r = 38$, $Q \times f = 23{,}700$ GHz (at 4.8 GHz), and $\tau_f = -3$ ppm/°C. The obtained bulk density of 5.11 g/cm^3 for $Ba_2Ti_3Nb_4O_{18}$ ceramic corresponded to 97% of the theoretical density (JCPDS #77–1205). Increasing sintering temperature resulted in a slight decrease in dielectric constant and $Q \times f$ values, which was perhaps due to the abnormal grain growth of $Ba_2Ti_3Nb_4O_{18}$ ceramics.

Fig. 3 shows the bulk densities of $Ba_2Ti_3Nb_4O_{18}$ ceramics with various additives (2 wt% MC; 1.5 wt% MC and 0.5 wt% LBS; 1 wt% MC and 1 wt% LBS; 0.5 wt% MC and 1.5 wt% LBS; 2 wt% LBS) as a function of temperature. It can be observed that a moderate increase and then a slight decrease in the bulk densities of samples with increasing the sintering temperature. However, the bulk densities decreased with increasing the content of LBS glass which was mainly due to the low density of LBS. Significantly, the bulk density of $Ba_2Ti_3Nb_4O_{18}$ sam-

Table 1
Densities and microwave dielectric properties of $Ba_2Ti_3Nb_4O_{18}$

Temperature (°C)	Density (g/cm^3)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
1190	5.03	38	23,700	–
1220	5.11	38	23,700	−3
1250	5.10	37	23,100	–
1280	5.08	35	22,800	−5
1310	5.01	35	22,100	–

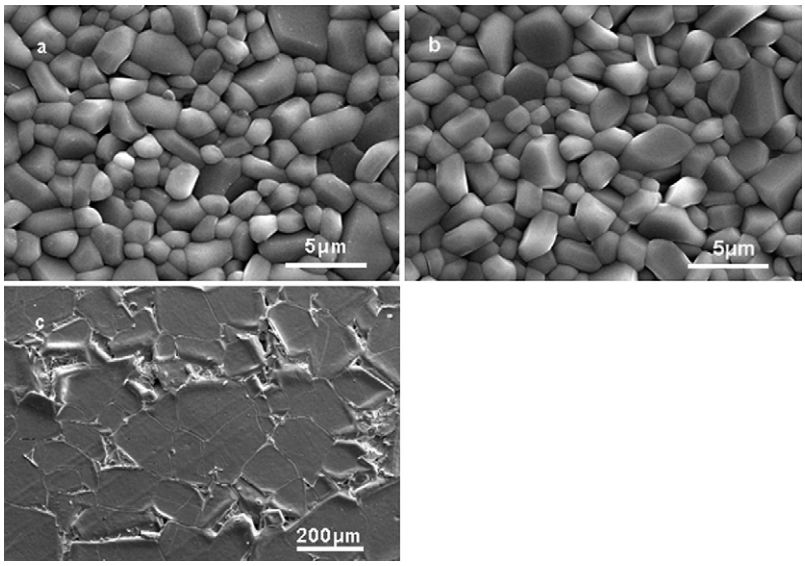

Fig. 2. SEM micrographs of $Ba_2Ti_3Nb_4O_{18}$ sintered at different temperatures for 2 h: (a) 1220 °C, (b) 1250 °C, and (c) 1310 °C.

ples with 2 wt% MC increased from 3.95 g/cm^3 to 5.10 g/cm^3 on increasing the temperature from 875 °C to 900 °C. The maximum density values of samples with MC and LBS reached above 97% of the theoretical density of $Ba_2Ti_3Nb_4O_{18}$ ceramics. These results revealed that additives of MC and LBS could remarkably lower the sintering temperature of $Ba_2Ti_3Nb_4O_{18}$ ceramics.

Fig. 4 shows the X-ray diffraction patterns of $Ba_2Ti_3Nb_4O_{18}$ with various contents of MC and LBS sintered at 900 °C for 2 h. It was evident that the main phase was $Ba_2Ti_3Nb_4O_{18}$ accompanied by second phase of $Ba_3Ti_4Nb_4O_{21}$ and unknown phase. In the previous study, $Ba_3Ti_4Nb_4O_{21}$ phase also existed in $Ba_3Ti_5Nb_6O_{28}$-based ceramics when CuO and B_2O_3 were added.[18] It indicated that a small amount of $Ba_3Ti_4Nb_4O_{21}$ would appear in $Ba_2Ti_3Nb_4O_{18}$ ceramics at low temperature and the cause was unclear yet. Moreover, it is worthy to note that the unknown phase was observed with 0.5 wt% MC and 1.5 wt% LBS and the peak intensities enhanced with increasing the contents of LBS additive. This phenomenon implied the unknown phase was related with LBS additive.

The SEM micrographs of $Ba_2Ti_3Nb_4O_{18}$ with various contents of MC and LBS sintered at different temperatures are shown in Fig. 5. $Ba_2Ti_3Nb_4O_{18}$ with 2 wt% MC sintered at 900 °C showed a dense microstructure without porosity. However, the presence of second phase, clearly distinguishable from the nearly rounded grains, was observed in Fig. 5a. The second phase along the grain boundary and triple junctions distributed uniformly for sample with 1 wt% MC and 1 wt% LBS sintered at 900 °C (Fig. 5b). With the sintering temperature increasing up to 950 °C, the platy second phase bestrewed the surface (Fig. 5d). $Ba_2Ti_3Nb_4O_{18}$ with 2 wt% LBS sintered at 900 °C became porous which indicated the sample did not densify at 900 °C as shown in Fig. 3. In order to exactly identify the compositions of the second phases in Fig. 5a, energy-dispersive

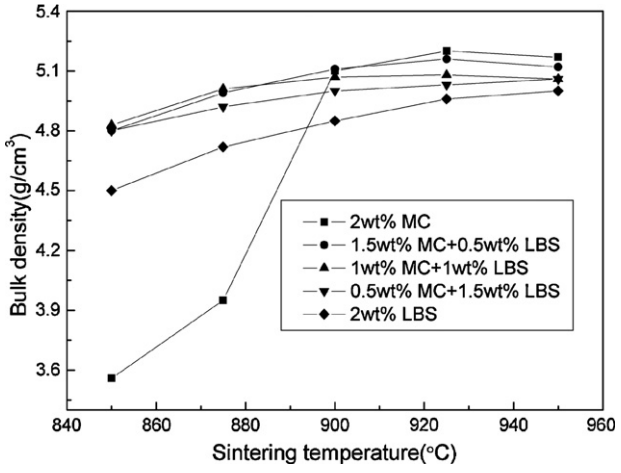

Fig. 3. Bulk densities of $Ba_2Ti_3Nb_4O_{18}$ ceramics with various additives sintered at different temperatures.

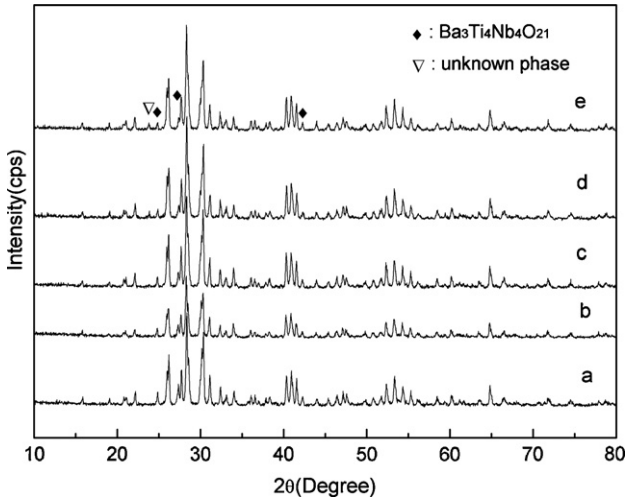

Fig. 4. XRD patterns of $Ba_2Ti_3Nb_4O_{18}$ ceramics with (a) 2 wt% MC, (b) 1.5 wt% MC + 0.5 wt% LBS, (c) 1 wt% MC + 1 wt% LBS, (d) 0.5 wt% MC + 1.5 wt% LBS, and (e) 2 wt% LBS sintered at 900 °C for 2 h.

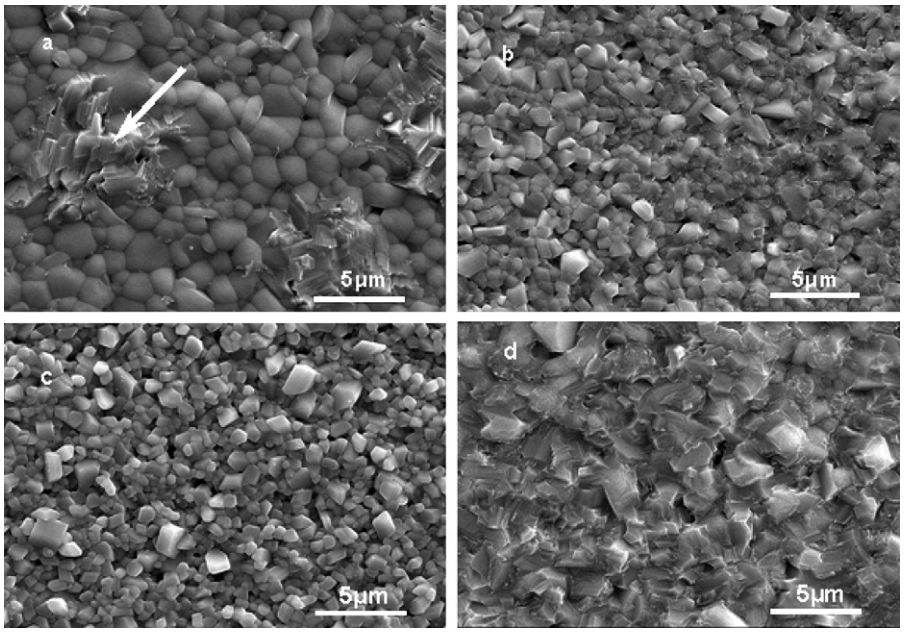

Fig. 5. SEM micrographs of $Ba_2Ti_3Nb_4O_{18}$ ceramics with (a) 2 wt% MC, (b) 1 wt% MC + 1 wt% LBS, (c) 2 wt% LBS sintered at 900 °C for 2 h and (d) 1 wt% MC + 1 wt% LBS sintered at 950 °C for 2 h.

spectroscopy (EDS) analysis has been performed. The result is given in Fig. 6. It was found that the second phase in Fig. 5a was a Cu-rich phase.

Fig. 7 shows the dielectric constant values of $Ba_2Ti_3Nb_4O_{18}$ with various contents of MC and LBS additives as a function of sintering temperature. The dielectric constant showed the same tendency as the bulk density. It is understood that a high density would lead to a high dielectric constant owing to lower porosity. The dielectric constant deceased with increasing LBS content which attributed to the ε_r of LBS glass is generally low.[19,20] It is noteworthy that ε_r of low-fired $Ba_2Ti_3Nb_4O_{18}$ ceramics with 1.5 wt% MC and 0.5 wt% LBS or 2 wt% MC was higher even than that of pure $Ba_2Ti_3Nb_4O_{18}$ densified fully. This can be explained by the fact that the presence of second phase $Ba_3Ti_4Nb_4O_{21}$ with a high ε_r (55).[14]

Fig. 8 illustrates the $Q \times f$ values of $Ba_2Ti_3Nb_4O_{18}$ (at 4.8 GHz) with various contents of MC and LBS additives as a function of sintering temperature. For almost all the specimens, with increasing the sintering temperature, the $Q \times f$ values increased and reached a maximum value and then decreased. The degradation of the $Q \times f$ values was probably due to increasing the second phase caused by increasing sintering temperature as shown in Fig. 5d. It is interesting that the $Q \times f$ values of $Ba_2Ti_3Nb_4O_{18}$ samples with 2 wt% MC or 2 wt% LBS are quite low, but the $Q \times f$ values could be improved remarkably with MC and LBS combined additives, especially with 1.5 wt% MC and 0.5 wt% LBS. As shown in Fig. 8, the saturated $Q \times f$ value decreased quickly from 15,000 GHz (at 900 °C) with 1.5 wt% MC and 0.5 wt% LBS to 5800 GHz (at 950 °C) with 2 wt%

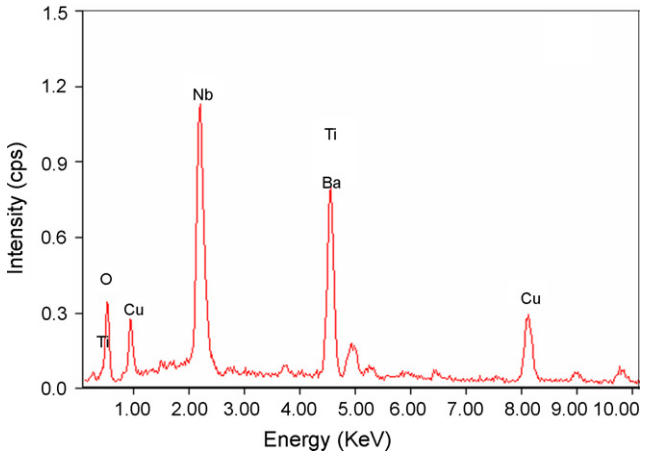

Fig. 6. Energy spectrum analysis of $Ba_2Ti_3Nb_4O_{18}$ ceramics with 2 wt% MC sintered at 900 °C for 2 h.

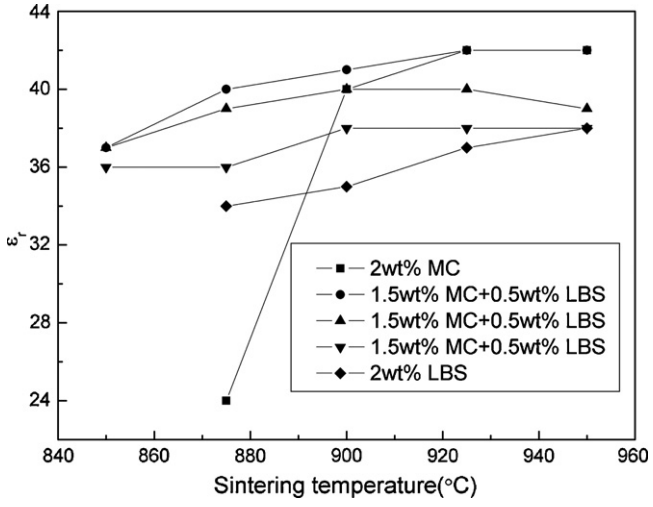

Fig. 7. Dielectric constants of $Ba_2Ti_3Nb_4O_{18}$ ceramics with various contents of MC and LBS sintered at different temperatures.

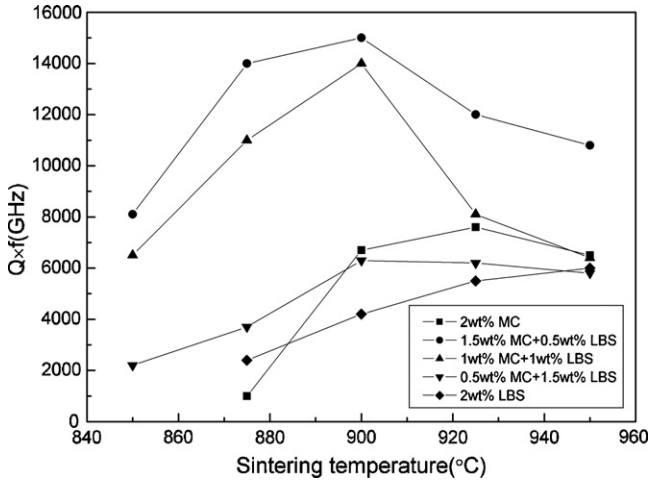

Fig. 8. The $Q \times f$ values of $Ba_2Ti_3Nb_4O_{18}$ samples with various amounts of MC and LBS sintered at different temperatures.

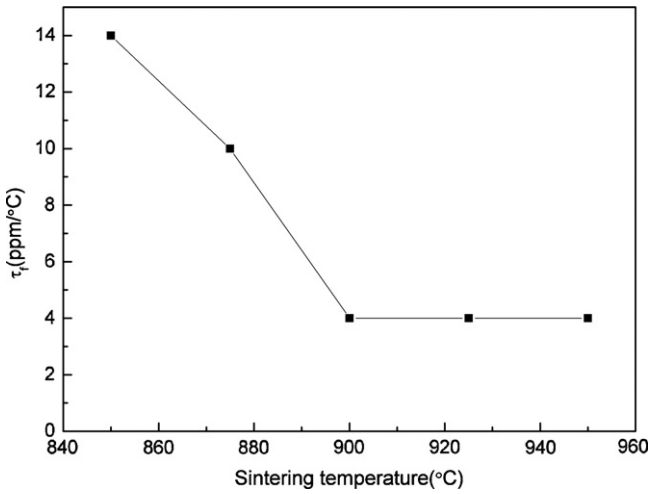

Fig. 9. The τ_f of $Ba_2Ti_3Nb_4O_{18}$ sample with 1.5 wt% MC and 0.5 wt% LBS sintered at different temperatures.

LBS. The above results clearly indicated that the presence of a small amount of LBS effectively enhanced the $Q \times f$ value of $Ba_2Ti_3Nb_4O_{18}$ sample with singly MC. The probable cause is that the presence of LBS distributed Cu-rich phase evenly throughout the samples. However, further addition of LBS was detrimental to the $Q \times f$ value, which perhaps attributed to the generation of the unknown phase as shown in Fig. 4.

Fig. 9 shows the temperature coefficient of the resonant frequency of $Ba_2Ti_3Nb_4O_{18}$ samples with 1.5 wt% MC and 0.5 wt% LBS as a function of sintering temperature. As shown in Table 1, the pure $Ba_2Ti_3Nb_4O_{18}$ has a negative τ_f. In contrast, the $Ba_3Ti_4Nb_4O_{21}$ has a large positive τ_f, which results in the increase of τ_f in low-fired $Ba_2Ti_3Nb_4O_{18}$ with 1.5 wt% MC and 0.5 wt% LBS. It was also observed that the τ_f values shifted from 14 ppm/°C to 4 ppm/°C with temperature increasing from 850 °C to 900 °C. This can be explained by the fact that the $Ba_2Ti_3Nb_4O_{18}$ densified with increasing sintering temperature as shown in Fig. 3.

For application as LTCC, the X-ray diffraction patterns of 20 wt% Ag added $Ba_2Ti_3Nb_4O_{18}$ with 1.5 wt% MC and 0.5 wt% LBS sintered at 900 °C for 2 h is shown in Fig. 10. It can be observed that there are $Ba_2Ti_3Nb_4O_{18}$, $Ba_3Ti_4Nb_4O_{21}$ and Ag phases. This result implied no chemical reaction have taken place between the $Ba_2Ti_3Nb_4O_{18}$ ceramics and the electrode material. Moreover, Fig. 11 shows SEM micrographs and EDS

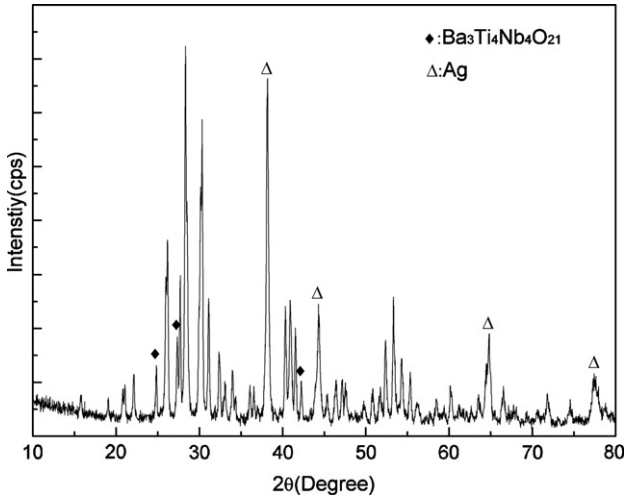

Fig. 10. XRD patterns of 20 wt% Ag added $Ba_2Ti_3Nb_4O_{18}$ with 1.5 wt% MC and 0.5 wt% LBS sintered at 900 °C for 2 h.

line scan of the interface between the silver electrode and $Ba_2Ti_3Nb_4O_{18}$ ceramics with 1.5 wt% MC and 0.5 wt% LBS tape co-fired at 900 °C for 2 h. The silver profile decreased sharply at the interface in Fig. 11, which indicated that the reaction of low-fired $Ba_2Ti_3Nb_4O_{18}$ ceramics with silver electrode

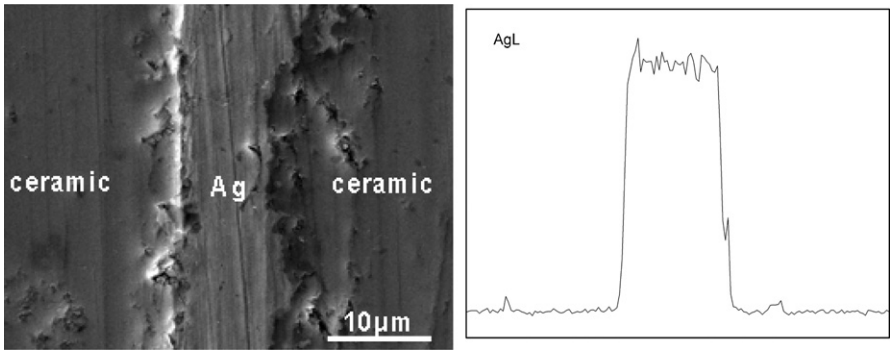

Fig. 11. EDS line scan of the interface between a silver electrode and ceramic body.

did not occur. Therefore, $Ba_2Ti_3Nb_4O_{18}$ ceramics with 1.5 wt% MC and 0.5 wt% LBS combined additives could be selected as a promising candidate for LTCC application.

4. Conclusions

In this study, the effects of $MnCO_3$–CuO and Li_2O–B_2O_3–SiO_2 glass on the sintering behavior, microstructures and microwave dielectric properties of $Ba_2Ti_3Nb_4O_{18}$ ceramics have been investigated in order to develop a new LTCC material. The sintering temperature of $Ba_2Ti_3Nb_4O_{18}$ ceramics decreased from 1220 °C to 900 °C when MC and LBS were added. The saturated dielectric constant (ε_r) increased and the temperature coefficient shifted to a positive value with the addition of MC and LBS, which were mainly due to the presence of the second phase $Ba_3Ti_4Nb_4O_{21}$. A dense $Ba_2Ti_3Nb_4O_{18}$ ceramic doped with 1.5 wt% MC and 0.5 wt% LBS is obtained when sintered at 900 °C for 2 h, which showed dielectric properties: $\varepsilon_r = 41$, $Q \times f = 15{,}000$ GHz (at 4.8 GHz), and $\tau_f = 4$ ppm/°C. Also, this material was compatible with Ag electrodes, which made it a promising ceramic for LTCC application.

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