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Ceramics International 35 (2009) 637–641
CERAMICS INTERNATIONAL
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# Silver cofirable $(Ca_{0.9}, Mg_{0.1})SiO_3$ microwave dielectric ceramics with $Li_2CO_3$–$Bi_2O_3$ additive

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Received 19 July 2007; received in revised form 29 July 2007; accepted 24 January 2008
Available online 24 April 2008

**Abstract**

The effects of $Li_2CO_3$–$Bi_2O_3$ (LB) additive on the microstructure, phase formation, microwave dielectric properties and applicability for low-temperature co-fired ceramics (LTCC) technology of $(Ca_{0.9}Mg_{0.1})SiO_3$ (CMS) ceramics were investigated. The sintering temperature of the CMS ceramics was reduced from 1290 °C to 890 °C by the addition of LB. Secondary phases $SiO_2$ and $Bi_4(SiO_4)_3$ were detected when LB content was less than 9 wt%. Low melting point liquid phases were formed when LB content was 11–14 wt%. The $Q_f$ value initially increased with the addition of LB and attained the maximum value for the 9 wt% LB-doped CMS ceramic. When the LB content exceeded 9 wt%, the $Q_f$ value decreased because of the presence of liquid phase and abnormal growth of grains. $\varepsilon_r$ of 6.92, $Q_f$ of 27,600 GHz and $\tau_f$ of −43.6 ppm/°C were obtained for 9 wt% LB-doped CMS ceramics sintered at 890 °C for 2 h. Also the ceramics can be well co-fired with Ag electrode.


*Keywords:* A. Tape casting; A. Sintering; C. Dielectric properties

## 1. Introduction

Microwave applications have made remarkable progress as advanced wireless communication systems have developed. The high operating frequency and miniaturization of multilayer components in these applications require dielectric materials with low dielectric constant ($\varepsilon_r$), high quality factor ($Q_f$) and stable temperature coefficient of the resonant frequency ($\tau_f \leq \pm 10$ ppm/°C) [1]. In the case of multilayer microwave integrated devices, low sintering temperatures for the dielectric ceramics, lower than the melting point of Ag (961 °C), are also required to develop the low-temperature co-fired ceramics (LTCC) [2,3]. In recent years, several material systems of low $\varepsilon_r$ such as $Zn_2SiO_4$, $AWO_4$ (A = Mg, Zn, Ca, Ni, Co), $A_3(VO_4)_2$ (A = Ca, Zn, Ba), $Li_3AlB_2O_6$ and $A_2P_2O_7$ (A = Ca, Sr, Ba; Mg, Zn, Mn) have been developed. However, because of their high sintering temperature, large $\tau_f$ value, incompatibility with Ag or environment pollution problem, etc., it is difficult for them to be applied in microwave component application [4–12].

Recently, we reported that $(Ca_{0.9}Mg_{0.1})SiO_3$ (CMS) ceramic sintered at 1290 °C for 2 h shows excellent microwave dielectric properties of $\varepsilon_r = 6.49$, $Q_f = 62{,}420$ GHz, and $\tau_f = -43.3$ ppm/°C [13]. In order to develop CMS ceramic as a candidate material for high-frequency multilayer devices, it is essential to reduce the sintering temperature of the ceramic available to the co-firing with Ag.

In this paper, we made the efforts on studying the effect of $Li_2CO_3$–$Bi_2O_3$ (LB) additive on the sintering character and microwave dielectric properties of CMS ceramic. Moreover, the structure of tape casting CMS ceramic sheet and the compatibility of the ceramic sheet with Ag electrode were investigated.

## 2. Experimental procedure

CMS ceramics with $x$LB ($5 \leq x \leq 14$ wt%) were prepared using conventional solid-state synthesis. MgO (99.0%), $CaCO_3$ (99.0%), $SiO_2$ (98.0%), $Li_2CO_3$ (98.0%) and $Bi_2O_3$ (99.0%) were used as starting materials. The powders were weighed according to the stoichiometric ratio of CMS, and milled with $ZrO_2$ balls for 24 h in ethanol. The mixtures were dried and calcined at 1100 °C for 4 h, then re-milled for 24 h with the addition of LB. With 5 wt% PVA solution as a binder, the

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0272-8842/$34.00 
doi:10.1016/j.ceramint.2008.01.019

powders were pressed into pellets with 18 mm in diameter and 8–10 mm in thickness under the pressure of 200 kg/cm$^2$. These pellets were sintered from 870 °C to 930 °C for 2 h.

The crystalline phases were identified by means of the powder X-ray diffraction analysis (XRD, D/max-RA, Rigaku) using Cu Kα radiation from 20° to 80° in 2$\theta$. Polished surface of the sintered specimens was observed using scanning electron microscope (SEM, JSM–5610LV). The EDS was measured with an energy-dispersive X-ray spectroscopy (EDS, EDAX GENENIS 4000). The bulk density (ρ) of the ceramics was measured by the Archimedes method. Microwave dielectric properties of the specimens were measured by the Hakki–Coleman dielectric resonator method using an Agilent 8719ET (0.05–13.5 GHz) Network Analyzer. The temperature coefficient of resonant frequency ($\tau_f$) at microwave frequencies was measured in the temperature range of 25–80 °C. The $\tau_f$ value (ppm/°C) can be calculated from the equation [14]:

$$\tau_f = \frac{f_{t_2} - f_{t_1}}{(t_2 - t_1) f_{t_1}} 10^6 \ \text{(ppm/°C)} \quad (1)$$

where $f_{t_1}$ and $f_{t_2}$ represent the resonant frequency at temperature $t_1$ and $t_2$, respectively.

## 3. Results and discussions

Powder X-ray diffraction patterns of the CMS ceramics doped with $x$LB ($5 \le x \le 14$ wt%) sintered at 890 °C for 2 h are shown in Fig. 1. XRD diffraction patterns of the specimens with 5 wt% and 7 wt% LB showed peaks indexed to $CaSiO_3$ as the main crystalline phase and $SiO_2$ as the secondary phase. When the LB content increased to 9 wt%, $Bi_4(SiO_4)_3$ as a secondary phase was formed. Further increasing the LB contents, specimens with $x = 11$–14 wt% turned to $CaSiO_3$ single-phased. The ion radii of $Mg^{2+}$, $Li^+$, $Ca^{2+}$ and $Bi^{3+}$ are 0.065 nm, 0.060 nm, 0.099 nm and 0.098 nm, respectively. For specimens with $x < 9$ wt%, $Li^+$ and $Bi^{3+}$ ions substituted $Mg^{2+}$ and $Ca^{2+}$ to form solid solutions. When the LB content

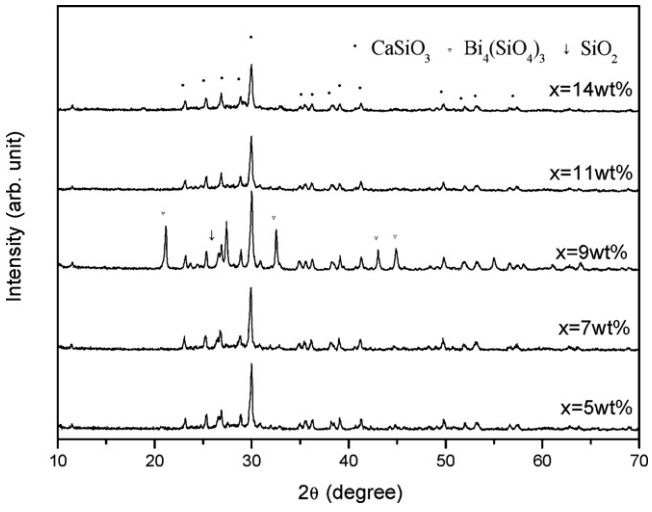


Fig. 1. Powder X-ray diffraction patterns of the CMS ceramics doped with $x$LB ($5 \le x \le 14$ wt%) sintered at 890 °C for 2 h.

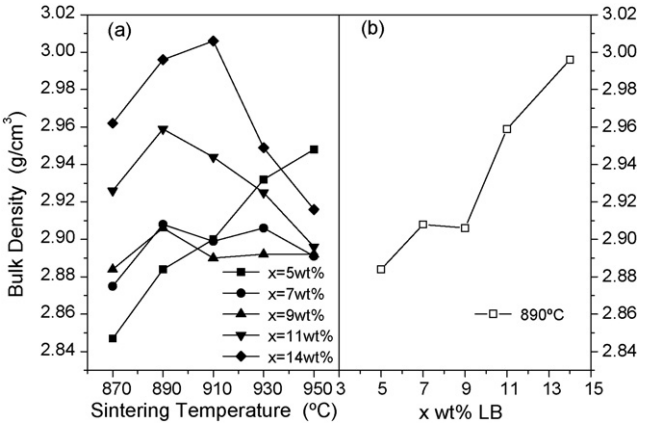


Fig. 2. Bulk density of the CMS ceramics doped with $x$LB ($5 \le x \le 14$ wt%) sintered at (a) various temperatures and (b) at 890 °C for 2 h.

increased to 9 wt%, the excessive $Bi^{3+}$ ions reacted with $SiO_2$ to form $Bi_4(SiO_4)_3$. When the LB content increased from 11 wt% to 14 wt%, the amount of low melting point liquid phase was sufficient to be observed by SEM as shown in Fig. 3(f). As a result, the intensity of peaks indexed $CaSiO_3$ decreased with the increasing amount of liquid phase. It indicated that the liquid phase had excellent wettability with $CaSiO_3$ particles.

Fig. 2a shows the bulk densities of the CMS ceramics doped with $x$LB ($5 \le x \le 14$ wt%) sintered at various temperatures for 2 h. The density of the CMS with 5 wt% LB was remarkably increased with increasing sintering temperature. When more additives were doped, the density of the specimens with 7–14 wt% LB was initially increased with sintering temperature up to 890 °C but decreased at higher temperatures. We can draw the conclusion that specimens with 7–14 wt% LB could be well sintered at 890 °C while those with 5 wt% LB could not be densified even sintered at 950 °C. Densities of the specimens sintered at 890 °C were increased with the LB content as shown in Fig. 2b. The increase of density was mainly owed to the increasing content of $Bi_2O_3$, which has high density of 8.90 g/cm$^3$.

SEM micrographs of the CMS ceramics doped with $x$LB ($5 \le x \le 14$ wt%) sintered at 890 °C for 2 h are shown in Fig. 3(a–e). For specimens with 5–9 wt% LB, which had secondary phases as shown in the XRD patterns (Fig. 1), the change of grain size was unobvious. It can be considered that the growth of grains was restrained by the secondary crystal phases. Increasing the LB content from 11 wt% to 14 wt%, the grain size of the specimens obviously increased as shown in Fig. 3(d) and (e). The morphology of grain surface of the specimen with 14 wt% LB sintered at 890 °C was covered with liquid phases, which improved the sintering character of the ceramics and led to the growth of the crystal grains. Compared with the microstructure of high-temperature sintered specimens [13], grains of LB-doped CMS ceramics exhibited two shapes: large rod-like grains and small variform grains. Table 1 shows the semi-quantitative EDS analysis of specimens with 14 wt% LB. It was found that the analyzed composition of large grains like spectra 1 were nearly equal to the stoichiometric ratio of $(Ca_{0.9}, Mg_{0.1})SiO_3$. The small grains like spectra 2 contained

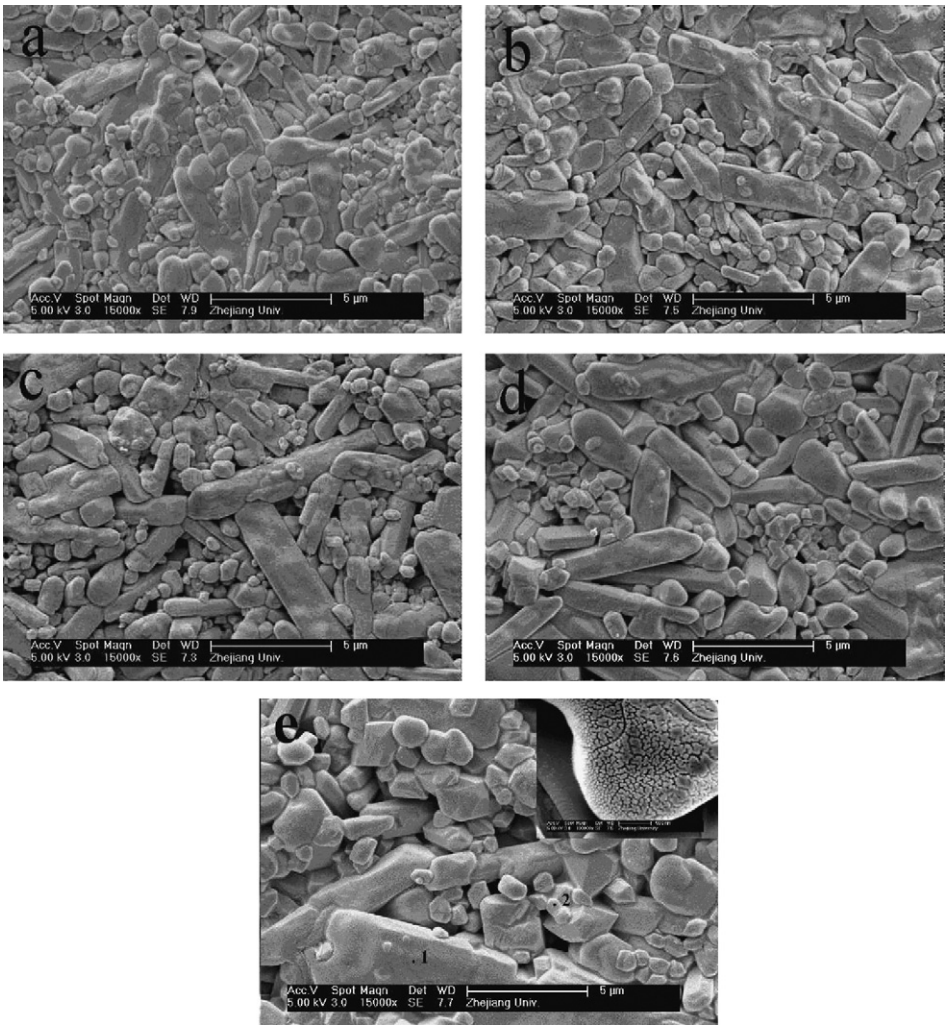


Fig. 3. SEM micrographs of the CMS ceramics doped with $x$LB ($5 \leq x \leq 14$ wt%) sintered at 890 °C for 2 h: (a) $x = 5$ wt%, (b) $x = 7$ wt%, (c) $x = 9$ wt%, (d) $x = 11$ wt% and (e) $x = 14$ wt%.

more Mg than the large ones. It indicated that the increase of $Mg^{2+}$ could restrain the growth of the grains.

Fig. 4 shows the microwave dielectric properties of the CMS ceramics doped with $x$LB ($5 \leq x \leq 14$ wt%) as a function of sintering temperature. The variation of the $\varepsilon_r$ and $Q_f$ value was similar to that of the bulk density. For specimens with 5 wt% LB, the value of $\varepsilon_r$ increased with the sintering temperature. When $x > 5$ wt%, $\varepsilon_r$ of the specimens reached the maximum value at 890 °C. It has been reported that $Q_f$ value is affected by the secondary phase, density, impurities and grain size. As shown in Fig. 4, the $Q_f$ value of the specimens considerably increased and then decreased with the increasing addition of LB. The maximum $Q_f$ value was obtained for the 9 wt%

Table 1
SEM–EDS results for 14 wt% LB-doped CMS ceramic sintered at 890 °C for 2 h

| | Element | | | |
|---|---|---|---|---|
| | Mg (At%) | Ca (At%) | Si (At%) | Bi (At%) |
| Spectra 1 | 03.53 | 44.15 | 50.01 | 02.32 |
| Spectra 2 | 16.08 | 28.58 | 53.20 | 01.87 |

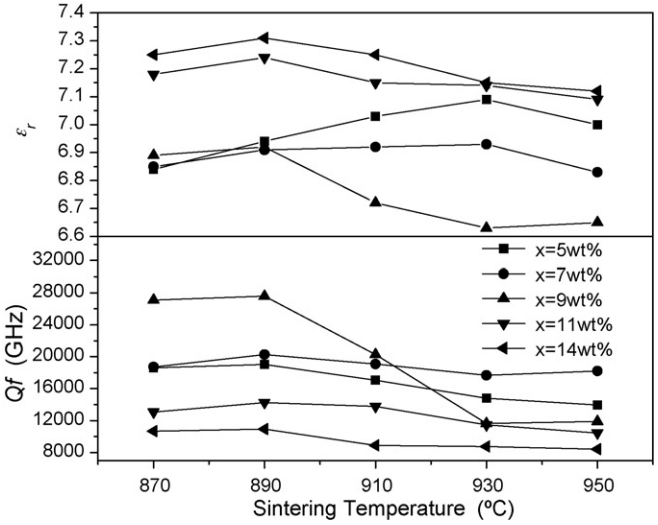


Fig. 4. Microwave dielectric properties of the CMS ceramics doped with $x$LB ($5 \leq x \leq 14$ wt%) sintered at various temperatures for 2 h.

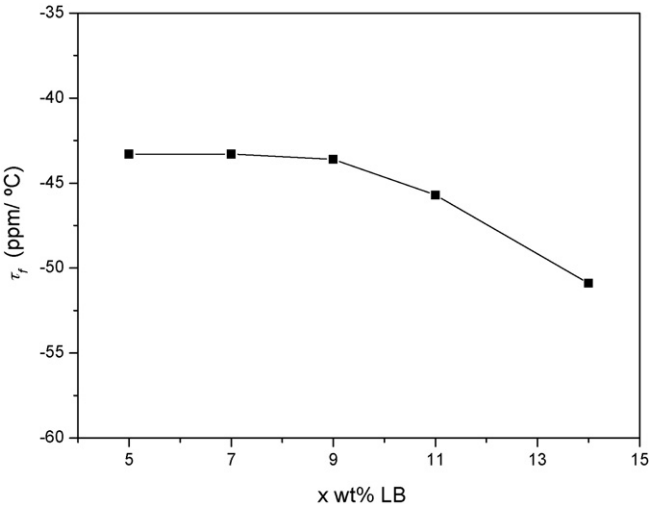


Fig. 5. $\tau_f$ values of the CMS ceramics doped with $x$LB ($5 \leq x \leq 14$ wt%) sintered at 890 °C for 2 h.

LB-doped CMS ceramics sintered at 890 °C. For specimens with $x < 9$ wt%, the increase of $Q_f$ value could be mostly attributed to the decrease of $SiO_2$ phase which has a lower $Q_f$ value. Specimen with 9 wt% LB contained $CaSiO_3$ and $Bi_4(SiO_4)_3$ as the main phase accompanied with small amount of $SiO_2$. As a result, it exhibited the maximum $Q_f$ value. For specimens with LB content exceeded 9 wt%, the $Q_f$ value considerably decreased due to the formation of liquid phases and abnormal growth of the grains. The low-temperature sintered ceramics have much lower $Q_f$ values (not more than 27,600 GHz as shown in Fig. 4) in comparison with the high-temperature sintered specimens (62,420 GHz) [13]. The inferiority of $Q_f$ value could be caused by the existence of liquid phases. Moreover, the morphology inhomogeneity in the main phase of the low-temperature sintered ceramics could also lead to the decrease of $Q_f$ value. The temperature coefficient of resonant frequency ($\tau_f$) of the LB-doped CMS ceramics sintered at 890 °C was also measured, as shown in Fig. 5. The $\tau_f$ value showed a considerable decrease for $11 \leq x \leq 14$ wt% due to the increasing amount of liquid phases. According to the above results, the CMS ceramic with 9 wt% LB additive sintered at 890 °C for 2 h showed good microwave dielectric properties of $\varepsilon_r = 6.92$, $Q_f = 27{,}600$ GHz, and $\tau_f = -43.6$ ppm/°C. Therefore, LB demonstrated strong potential as an additive for the low-temperature sintering of the microwave ceramics and the LB-doped CMS ceramic is a promising candidate material for low-temperature co-fired ceramics.

In order to investigate the applicability of CMS ceramics for LTCC technology, the tape casting process and the interface of 9 wt% LB-doped CMS ceramic sheet with Ag electrode were studied. The powder of CMS with 9 wt% LB was first mixed with solvents and dispersants in a ball mill for 16 h, and then plasticizers and binders were added and mixed for another 2 h to obtain the slurry. After tape casting and drying, the green tapes were obtained [15,16]. SEM micrograph of the surface of green tape is shown in Fig. 6. In the green tape, the average particle size is all less than 2 μm. There were no agglomerates

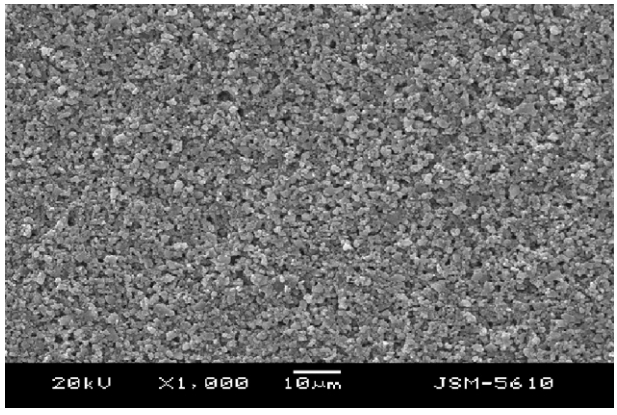


Fig. 6. SEM micrograph of the CMS green tape.

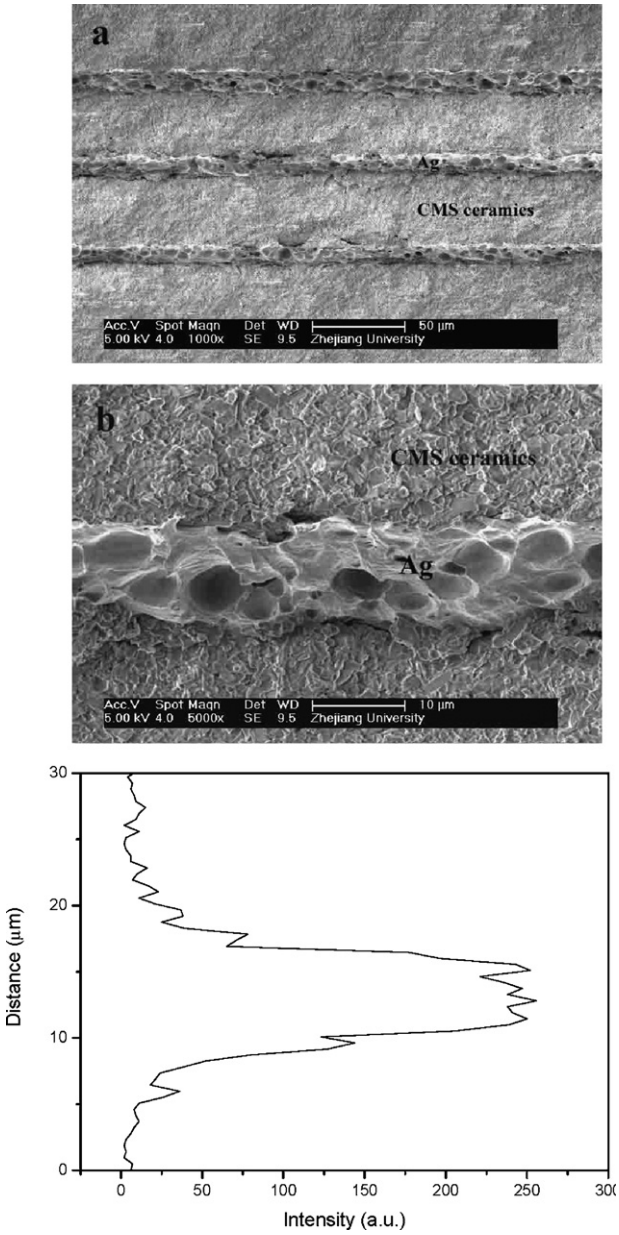


Fig. 7. SEM micrographs of (a) the interfacial microstructure of (LB-doped CMS)/Ag in a LTCC component and (b) the corresponding Ag distribution.

and a fine microstructure with small pores distributed homogeneously was found in the green body. It can be seen that a uniformly green density was achieved by the tape casting process.

Fig. 7 shows SEM micrographs of the interface of 9 wt% LB-doped CMS ceramic sheet with Ag electrode in a LTCC component and the corresponding Ag distribution. A few small cracks existed at the interface between the ceramic layer and the electrode layer. Several explanations concerning these interfacial cracks or delaminations have been put forth elsewhere [17,18], including green tape delaminations, rapid evolution of gas and heat release during burnout, and mismatched physicochemical properties between the electrode and the ceramic. In Fig. 7, it can be obviously observed that cracks at the interface between the ceramic layer and the electrode layer were rather small and there were a large amount of pores in the Ag electrode layers. Consequently it can be concluded that the rapid volatilization of additives in the ceramics and Ag slurry may be responsible for these interfacial defects. The element distribution of Ag is also shown in Fig. 7(b). It can be seen that Ag was only distributed in the central conductor region and did not diffuse to the ceramic region. On all accounts, we can draw the conclusion that the LB-doped CMS ceramics can well matched with Ag electrode.

## 4. Conclusions

The sintering temperature of the CMS ceramics can be effectively reduced from approximately 1290 °C to 890 °C when the LB additives were added. The $SiO_2$ and $Bi_4(SiO_4)_3$ secondary phases, which existed in the 5–9 wt% LB-doped CMS ceramics, disappeared with the increasing amount of LB. The phase composition plays an important role in determining the dielectric properties of the specimens. Typically, $\varepsilon_r$ of 6.92, $Q_f$ of 27566 GHz and $\tau_f$ of −43.6 ppm/°C were obtained for 9 wt% LB-doped CMS ceramics sintered at 890 °C for 2 h. Ag did not diffuse to the ceramic region when it was co-fired with the LB-doped CMS ceramic. It was proved that the LB-doped CMS ceramic is a promising candidate material for LTCC applications.

## Acknowledgement

This work was supported by Zhejiang Province Key Sci. and Tech. Program under grant No. 2006C11119.

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