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# The co-fired behaviors between Ag and glass–ceramics materials in LTCC

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**Abstract** The paper studied the interfacial co-fired behavior between silver and Ba–Ti–B–Si–O glass–ceramics composites for LTCC application. The dielectric properties of this LTCC glass–ceramic materials were as follows: $\varepsilon \approx$ 8–10, $\tan\delta \leq 2 \times 10^{-3}$ (at 1 GHz), and its sintering temperature was lower than 900 °C. The Ag elemental distribution near the interface between glass–ceramics and Ag was investigated by scanning electronic microscopy and energy spectrum analysis. No de-lamination, camber and cracking were found between LTCC/Ag systems after firing at 810–900 °C for 2 h. The experimental results showed that the diffusion of silver was mainly decided by sintering temperature and microstructure of LTCC. Promoting densification of the LTCC can prevent Ag diffusion from co-fired interface.

**Keywords** Low-temperature co-fired ceramics (LTCC) · Glass–ceramics · Silver · Diffusion · Microstructure · EDS

## 1 Introduction

Low-temperature co-fired ceramic (LTCC) technology is a low-cost process for fabricating multi-layers ceramic structures, which possesses several advantages making it suitable for mass-market telecommunication applications [1, 2, 5–15]. LTCC has a number of advantages: (1) it has lower dielectric loss and controllable permittivity; (2) it is suitable to producing modules in low-cost SMT packages, including BGA technology; (3) it is to lead to high-density packaging, including integrated, printed resistors and capacitors; (4) it enables high yield, fast turnaround and reduced the size and cost of devices with three-dimension structures; (5) it has the possibility of fabricating fine conductive lines and spaces, small interconnect via, flexible 3-D designs and high dielectric layer counts, etc.

LTCC means that ceramics or glass materials should be sintered at lower temperature in order to be co-fired with lower melting point copper, silver, or gold. Recently, sintering temperature of dielectric materials below 900 °C became the main development current. Because the silver easy diffuse in sintering process when the sintering temperature exceeded 930 °C, and it maybe reduce or destroy the performance of components. But in fact, the sintering temperature of most ceramics materials is higher than 900 °C, aim for reducing the sintering temperature of LTCC systems, the LTCC systems always adopt the mode of ceramics plus glass or glass–ceramics to decrease sintering temperature so as to meet the requirements in applications for LTCC [4–10].

In this paper, the co-fireability between Ag electrode and LTCC materials was mainly investigated by TMA and SEM. The silver migration was observed by EDS when Ba–Ti–B–Si–O glass–ceramics composites were co-fired with a silver electrode, and the microstructure of this LTCC influenced on the silver diffusion was also studied.

## 2 Experimental procedure

A powders-calcined process with conventional mixed oxide (oxides at least 99.9% pure) is investigated in this

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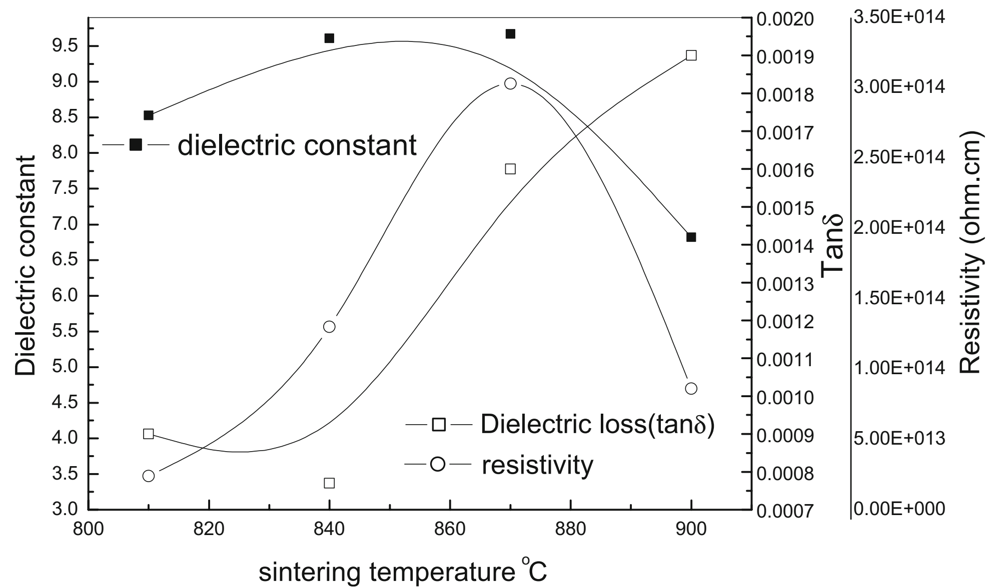


**Fig. 1** The relationship between dielectric properties (at 1,000 MHz) and DC specific resistance of LTCC and sintering temperature

experiment. In the processing, the calcined glass–ceramics composites, which consists of BaO:$TiO_2$ (rutile):$B_2O_3$:$SiO_2$ in the ratio of 28:20:10:42 wt.%, were calcined for 4 h at 750 °C in air. All glass–ceramic samples were prepared by a standard ceramics fabricated route; the BaO was imported by $Ba(OH)_2$, and $B_2O_3$ was imported by $H_3BO_3$. The samples were uniaxially pressed to form pellets (a little PVA binder is necessary) with LTCC powders, under a pressure of 4 MPa using a 10 mm diameter die. The thickness of the pressed sample is about 2 mm. The co-fired samples including Ag and glass–ceramics layers were fabricated by two-layers lamination, the procedure was first printing Ag paste on the surface of one pressed pellet, and then laminated another layer under suitable pressure. All samples were then sintered in air, at temperatures between 810 and 920 °C. The samples were all heated at a rate of 5 °C/min to the sintering temperature, sintered at corresponding temperature for 2 h, and then naturally cooled to room temperature, and removed from the furnace. The dielectric properties were measured by HP4991A analyzer after coated silver paste, and the resistivity was measured by HP4140B LCR analyzer.

## 3 Results and discussion

Dielectric loss is an important parameter of LTCC substrate, which characterizes the energy loss in circuit. The dielectric losses can be written in terms of the specific resistivity rate ($\rho$) at low frequency [3]:

$$\tan\delta = \frac{1}{(8.85 \times 10^{-14})2\rho\pi f \varepsilon_r} \quad (1)$$

Where the specific resistivity is given in Ωcm. As shown in formula 1, the dielectric losses should be inversely proportional to the specific resistivity, but in fact, the dielectric losses did not have any direct relationship with the specific resistivity as shown in Fig. 1. Therefore, the specific resistivity could be acting as an estimated index to dielectric losses in this LTCC materials system at high

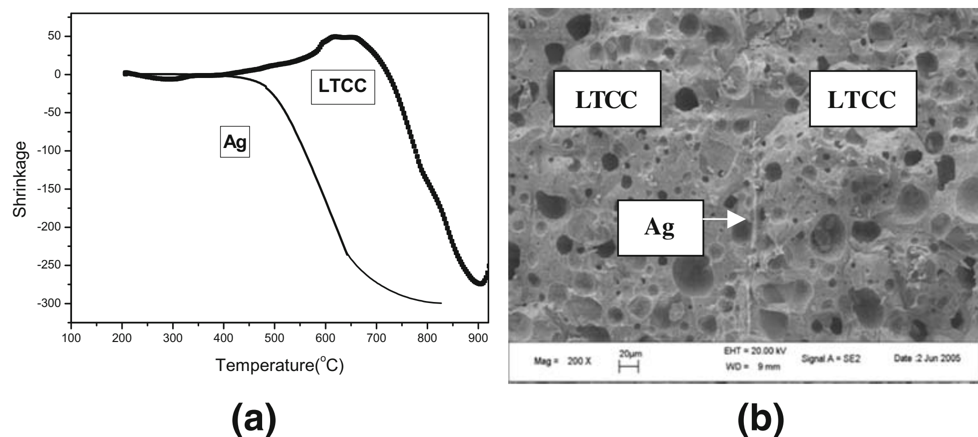


**Fig. 2** (**a**) The TMA shrinking curve of LTCC and silver electrode; (**b**) the co-fired interface between silver and LTCC sintered at 900 °C

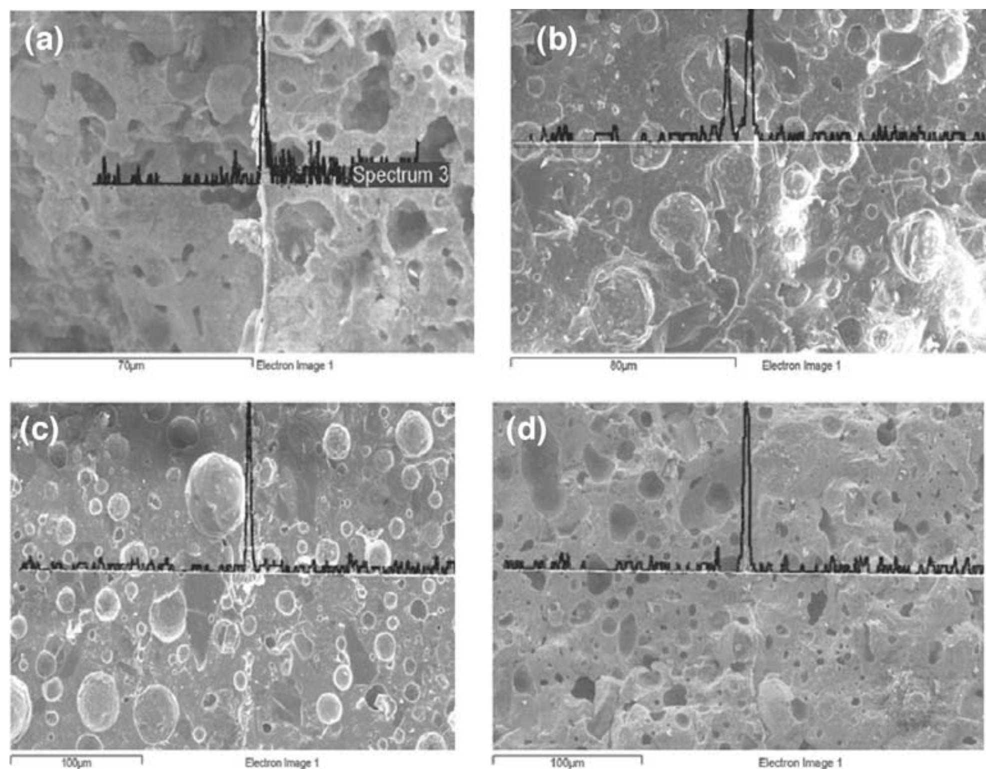


**Fig. 3** (**a**) The EDS analysis of Ag on the co-fired interface after being sintered at 840 °C; (**b**) at 870 °C; (**c**) at 900 °C; (**d**) at 920 °C

frequency that is unreasonable. The experimental results reveal that lower dielectric losses when the specific resistance rate of LTCC was larger than $10^{13}$ Ωcm. This LTCC materials have got high resistivity which results from the fact that the larger modifier ions (such as $Ba^{2+}$, etc.) fit in to plug up the migration paths through the lattice and decrease the ion migration in glass–ceramics LTCC system. In this study, the dielectric loss was only about 0.001–0.002 at 1,000 MHz measured by LCR analyzer, as shown in Fig. 1, which possess good application in domain of microelectronics packaging; moreover, the variety of dielectric losses did not have certainly relationship with the sintering temperature. It is believed that the phase composition changes could be found responsible for the changes of the losses, because the glass phases have higher losses than crystalline phases in the measured frequency range.

As shown in Fig. 1, the dielectric constant has been found to be increased with the sintering temperature increasing before 870 °C, the reason for this is that densification of LTCC becomes large so as to promote the dielectric constant. When sintering temperature exceeds 900 °C, the liquids phase in LTCC that would result in the deformation of sintered body, and then the densification becomes lower in value.

Research results showed the difficulties to different materials' co-fired technology to include: (1) the sintering temperature must be lower than ever so that it can co-fire with Ag electrode and control diffusion on the co-fired interface; (2) the heating stress, de-lamination, warp and crack at co-fired interface are easily developed because of the mismatch of different materials on the sintering temperature, sintering shrinkage, sintering shrinkage rate and thermal expanding coefficient; (3) the reaction and diffusion can influence the performance, reliability and microstructure of components [2, 3].

In LTCC, different materials, different sintering temperature, sintering processing and thermal expanding coefficient, were the major causes of this mismatch. However, investigating the LTCC/Ag co-fired samples, some defects such as camber, de-lamination, and cracks could be not

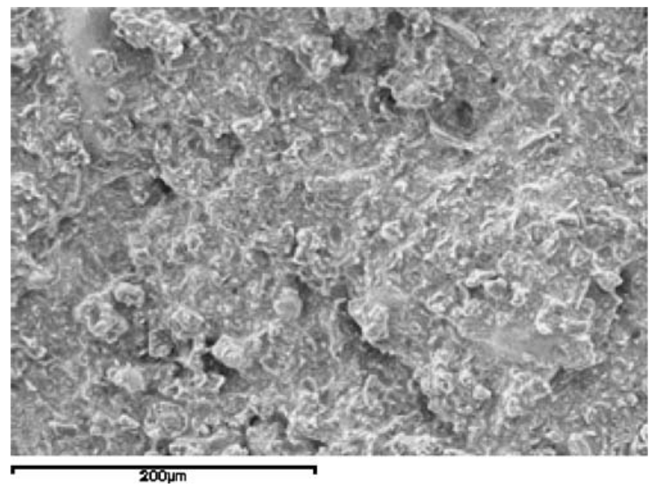


**Fig. 4** The fracture SEM photo of LTCC/$Al_2O_3$ sintered at 900 °C

found. The reason for this is that is due to the matched sintering kinetic between Ag and glass–ceramic. As shown in Fig. 2(a), the specimens of LTCC undertaken the effective densification range from 750 to 900 °C at a constant heating rate of 15 °C/min with TMA, and the linear shrinkage of glass–ceramic in the range of 10–15% was near the maximal value around temperature 900 °C. Therefore, around 900 °C was the best sintering temperature range. In addition, the shrinkage of LTCC was near the silver electrode, and densification rate of both materials may match the requirements of LTCC, which the delamination was not developed in sintering processing. Fig. 2(b) showed the co-fired interface between silver and LTCC, there were not mismatch phenomena such as delamination, cracking and camber in co-fired processing.

Usually, the decided factors on diffusion are temperature, time, element concentration and distance, but the premise that diffusing channel is exist in different system. Figure 3 is the EDS analysis of Ag with linear scan for different sintering temperature, 840, 870, 900 and 920 °C, respectively. The EDS results showed the Ag element diffusion that badly took place in sintering temperature of 840 °C but other samples did not take place. From the SEM photograph of co-fired interface as shown in Fig. 3(a), (b), (c) and (d), the microstructure of 840 °C were more heterogeneous than 870–920 °C because there was many connective pore in 840 °C. Hence, the existence of connective pore (but not glass–ceramic matrix) was the key cause of Ag diffusion. Almost Ag element cannot diffuse in this LTCC matrix so that the microstructure become main factors on diffusing in LTCC/Ag co-fired system. If the densification microstructure can be achieved for LTCC, the LTCC matrix would prevent Ag diffusion from co-fired interface to inner matrix. Experimental result showed the suitable alumina additive could promote the densification of LTCC. Figure 4 was the fracture SEM photo of LTCC with 5 wt% alumina. Obviously, the densification of LTCC/$Al_2O_3$ system was better than LTCC without alumina (as shown in Fig. 3), and the porous was completely eliminated after sintered at 900 °C/2 h. The Ag diffusion was not only prevented, but also the dielectric properties could hold steady for LTCC application.

## 4 Conclusions

No de-lamination, camber and cracking were found between Ba–Ti–B–Si–O glass–ceramics LTCC/Ag systems after firing at 810–900 °C for 2 h. The experimental results showed the diffusion of silver that was mainly decided by sintering temperature and microstructure of LTCC. Promoting densification of the LTCC can prevent Ag diffusion from co-fired interface.

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