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Suppression of Shrinkage Mismatch in Hetero-Laminates Between Different Functional LTCC Materials

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Abstract: Integrating dielectric materials into LTCC is a convenient method to increase the integration density in electronic circuits. To enable co-firing of the high-k and low-k dielectric LTCC materials in a multi-material hetero-laminate, the shrinkage characteristics of both materials should be similar. Moreover, thermal expansion mismatch between materials during co-firing should be minimized. The alternating stacking of an LTCC with silica filler and that with calcium-zirconate filler was observed to examine the use of the same glass in different LTCCs to minimize the difference in shrinkage and thermal expansion coefficient. For the LTCC of silica filler with a low dielectric constant and that of calcium zirconate filler with a high dielectric constant, the amount of shrinkage was examined through a thermomechanical analysis, and the predicted appropriate fraction of each filler was applied to green sheets by tape casting. The green sheets of different fillers were alternatingly laminated to the thickness of 500 ㎛. As a result of examining the junction, it was observed through SEM that a complete bonding was achieved by constrained sintering in the structure of ‘calcium zirconate 50 vol%-silica 30 vol%-calcium zirconate 50 vol%’.

Keywords: LTCC, Glass, Tape casting, Shrinkage

1. INTRODUCTION

The rapid development of wireless telecommunication and RF transmitter/receiver technology puts forward the requirement of electronic modules with high-integrated and high performance in microwave frequencies. The low temperature co-fired ceramics (LTCC), which are characterized by a three-dimensional package structure with embedded resistor-capacitor components, can significantly reduce the size and weight of microwave modules [1]. Low temperature co-fired ceramic (LTCC) has high insulation, excellent frequency characteristics and a thermal expansion coefficient similar to that of silicon, which has been considered as the most promising material for electronic substrates [2]. The LTCC materials comprising of 20 to 50 vol% of ceramic powders mixed with a majority low softening point glass phase in non-reactive systems, or little reaction between the ceramic fillers and the glass phase is observed, whereas in other cases the glass partially crystallizes or reacts with the ceramic powder and forms additional phases which contribute significantly to the final properties and specifications. The sintering of these LTCC materials is governed by a liquid-phase sintering mechanism including different stages, i.e., rearrangement, dissolution, precipitation, and skeletal sintering [3]. The integration of dielectric

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materials into LTCC is a convenient method to increase the integration density in electronic circuits. Usually a middle-k or high-k dielectric or relaxor material is integrated as screen-printed thick film or green tape in the multilayer architecture of the low-k LTCC tapes. In order to enable co-firing of the high-k and low-k dielectric LTCC materials in a multi-material hetero-laminate, the shrinkage characteristics of both materials should be very similar. Moreover, thermal expansion mismatch and chemical reactions between materials during co-firing should be minimized [4].

In this study, the alternating stacking of an LTCC with silica filler and that with calcium-zirconate filler was observed to examine the use of the same glass in different LTCCs to minimize the difference in shrinkage and thermal expansion coefficient. Through the results of various stacking designs, the feasibility of the use of the same glass was investigated.

2. EXPERIMENTAL PROCEDURE

The composition of the prepared glass is shown in Table 1. Mixtures were melted at 1,550°C for 30 minutes, cooled with a dry quenching roller at room temperature, and crushed. The crushed coarse powder was first pulverized with a disk mill, then passed through KS-#80 sieve, and second pulverized with a bead mill using ethanol for 5 hours, followed by passing through a KS-#325 sieve.

Silica (SiO_2, 99.5%, KORSIL K-10, 21st Century Silica Ltd., Korea) and calcium zirconate ($CaZrO_3$, 98%, CZ, Cepotech Co., Ltd., Korea) were selected as fillers.

Green sheets were prepared by tape casting. The organic content is shown in Table 2. Green bars were prepared as thick as 500 ㎛ with the use of individual green sheets of 50 ㎛. All laminates were manufactured by uniaxial thermal compression (80°C, 25MPa, 10 minutes). For shrinkage investigations, these laminates were cut into samples of 15 ㎜ × 30 ㎜ in size. The specimens were heated from room temperature to 600°C at 2°C/min rate, held for 1 hour to remove organics, and then heated to 870°C at 5°C/min rate, held for 1 hour for sintering. The stacking design is shown in Fig. 1.

Particle size analyses (LA-350, Horiba, Japan) of glass and filler powders were performed, and the dielectric constant of individual silica LTCC and calcium zirconate LTCC were measured using an impedance analyzer (E4991B, Agilent, USA). Thermomechanical analysis with TMA (Q400, TA instruments, USA) was operated with specimens. Specimens for TMA measurement were prepared with sizes of a diameter of 3 mm and a height of 5 mm by uniaxial press molding from mixing glass and filler powders without organics. The shrinkage was measured geometrically. The shape of each

Table 1. Glass composition.

Component	Mole ratio	Raw material	Purity	Manufacturer
SiO_2	69.9%	SiO_2	99.5%	Duksan, Korea
B_2O_3	17.9%	H_3BO_3	99.5%	Duksan, Korea
Al_2O_3	2.2%	Al_2O_3 (LS-130)	99.5%	Nikkei, Japan
K_2O	10.0%	K_2CO_3	99.0%	Duksan, Korea
Sum	100%	-	-	-

Table 2. Composition for tape casting.

Component		Ratio	Raw material	Purity	Manufacturer
LTCC	Glass	9.5 vol%	-	-	-
	Filler	6.3 vol%	-	-	-
Solvent	Ethanol	31.2 vol%	Ethanol	95.1%	Duksan, Korea
	Toluene	42.5 vol%	Toluene	99.5%	Duksan, Korea
Organics	Dispersant	0.3 vol%	BYK-111	-	BYK, Germany
	Binder	6.8 vol%	BM-SZ	-	Sekisui, Japan
	Plasticizer	3.4 vol%	Dibutyl phthalate	99.0%	Duksan, Korea
Sum		100.0 vol%	-	-	-

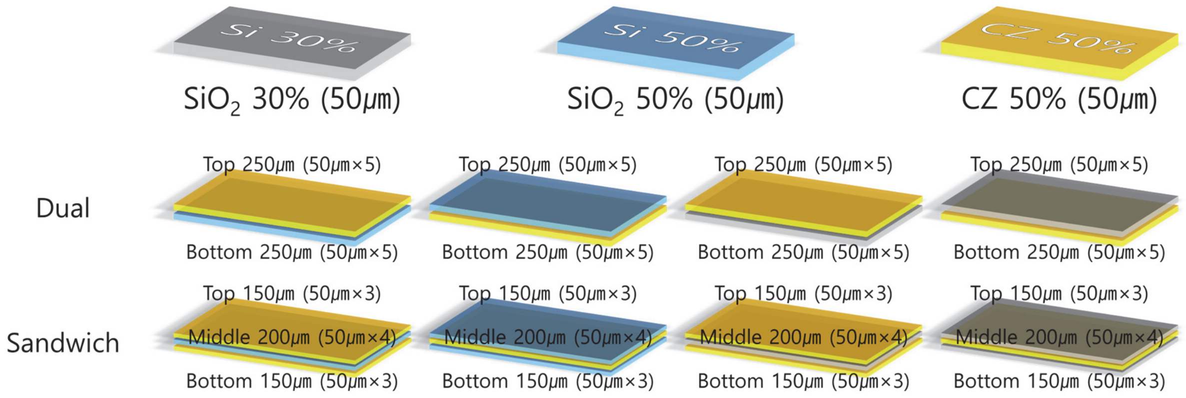


Fig. 1. Stacking designs for hetero laminates. 'Dual samples' are for cases of shrinkage constraining from the gravimetric force, and 'sandwich samples' are for cases of self-constraining.

powder and the microstructure of the sintered body were observed by SEM (AIS1800C, Seron Technologies Inc., Korea).

3. RESULTS AND DISCUSSIONS

Figure 2 shows the powder properties and SEM images of the prepared glass. It was observed that the average particle diameter was 6.8㎛ and had an irregular shape. Because it passed through KS-#325 sieve, abnormally large particles were not observed.

Figure 3 shows the powder properties and SEM images of the two selected fillers. Large particles of about 10 micrometers are observed to be mixed in silica, and huge aggregates are also thought to be present in particle size distribution. It was observed that aggregates are mixed in calcium zirconate.

The thermomechanical behavior according to the filler fraction is shown in Fig. 4. When the temperature was raised to 900°C, the final shrinkage amount for each filler increased as the glass content increased. As the dielectric properties are thought to be more apparent with the increase in the filler amount, calcium zirconate 50 vol%, silica 30 vol%, and 50 vol% were chosen. In the case of calcium zirconate 30 vol% (-64.55%) and silica 10 vol% (-71.67%) with large shrinkage amount, their slopes (expressed in the same unit as the coefficient of thermal expansion) from 800℃ to 900℃ are almost the same as -0.49%/℃. This is thought to indicate that the use of glass in common is effective. These behaviors are thought to indicate viscous mobility during sintering. Above the sufficiently high temperature, fluidities of large amounts of the same glass in the specimens are thought to dominate the shrinkage behaviors.

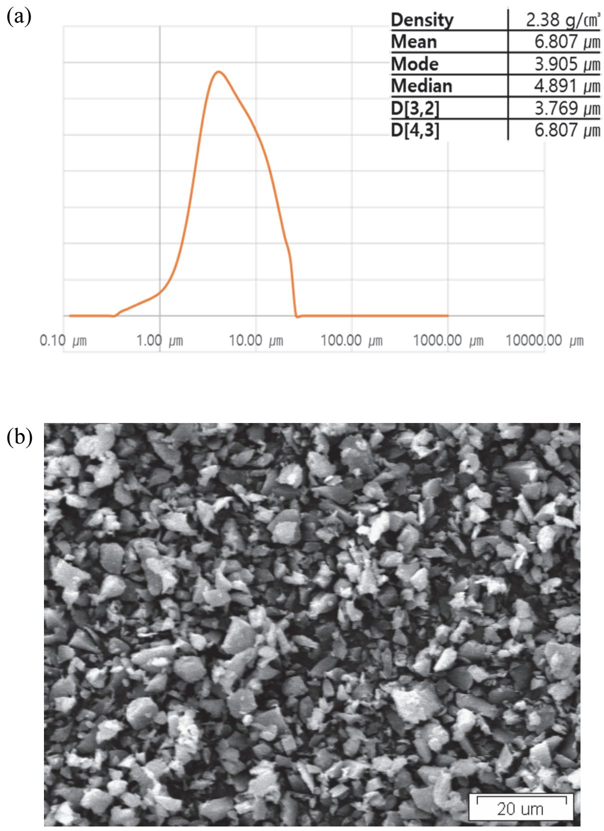
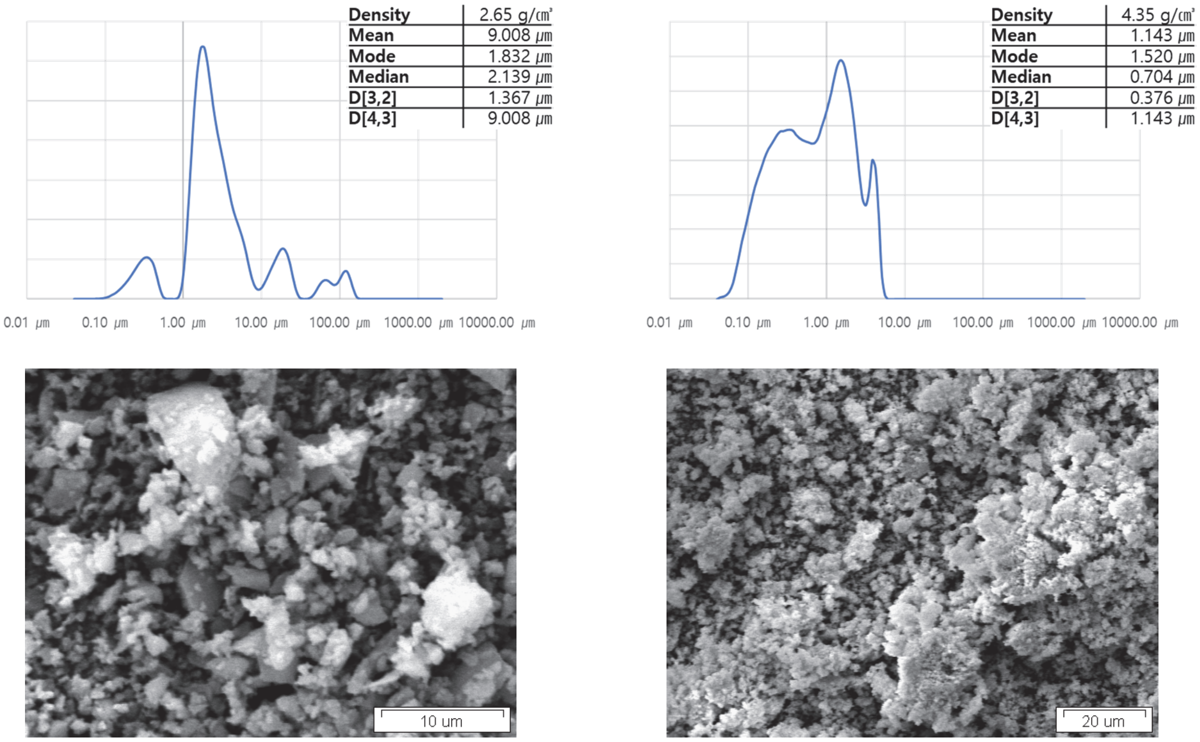


Fig. 2. Characteristics of prepared glass powder. (a) Particle size distribution and (b) SEM photo showing its shape.



(a) Silica (denoted as ‘SiO_2’)

(b) Calcium zirconate (denoted as ‘CZ’)

Fig. 3. Filler powders. (a) Particle size distribution (upper) and SEM photo (lower) of silica and (b) particle size distribution (upper) and SEM photo (lower) of calcium zirconate.

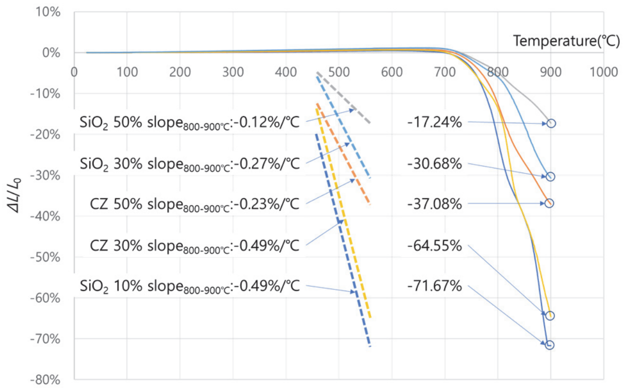


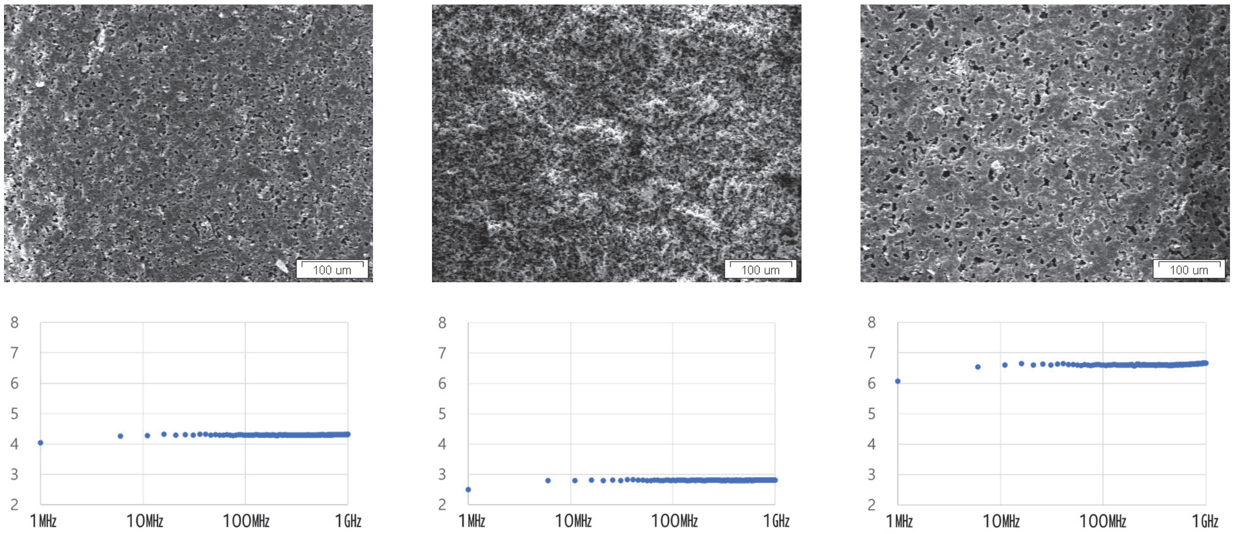
Fig. 4. Thermo-mechanical behaviors of various LTCCs with different fillers.

Figure 5 shows the microstructures and dielectric constants of sintered LTCC manufactured by tape casting for the three selected filler cases based on the thermomechanical analysis results. It can be observed that the higher the silica content, the lower the dielectric constant, as Lichterecker’s mixing rule predicts [5]. Lichterecker’s mixing rule is reported to be a useful practical formulation for determining the effective permittivity of homogenized dielectric mixtures as follows.

$$\log \varepsilon_m = V_h \log \varepsilon_h + V_l \log \varepsilon_l \tag{1}$$

ε_m	The relative dielectric constant of mixture
V_h	The volumetric ratio of a high-dielectric phase
ε_h	The relative dielectric constant of a high-dielectric phase
V_l	The volumetric ratio of a low-dielectric phase
ε_l	The relative dielectric constant of a low-dielectric phase

Figure 6 shows the shapes of the sintered laminates with different stacking designs. As the difference in shrinkage amounts between calcium zirconate 50 vol% and silica 30 vol% is smaller than that with silica 50 vol%, and the slope of 800~900℃ is also small in Fig. 4, the shrinkage stress during sintering was expected to be less. But, in (a) and (b), it is unusual that the shrinkage direction is different when calcium



(a) SiO_2 30 vol% (b) SiO_2 50 vol% (c) CZ 50 vol%

Fig. 5. Dielectric constants of LTCCs with two filler powders [SEM photos showing their microstructures (upper) in sintered bodies].

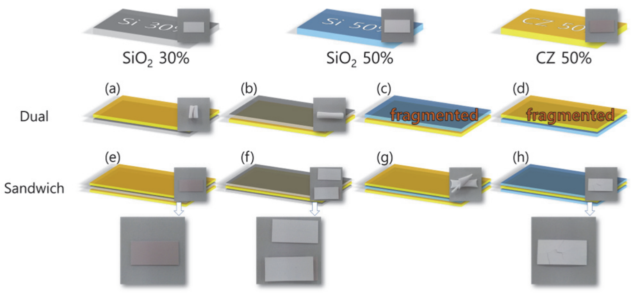
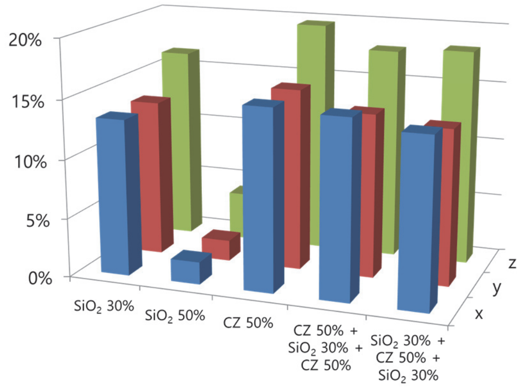


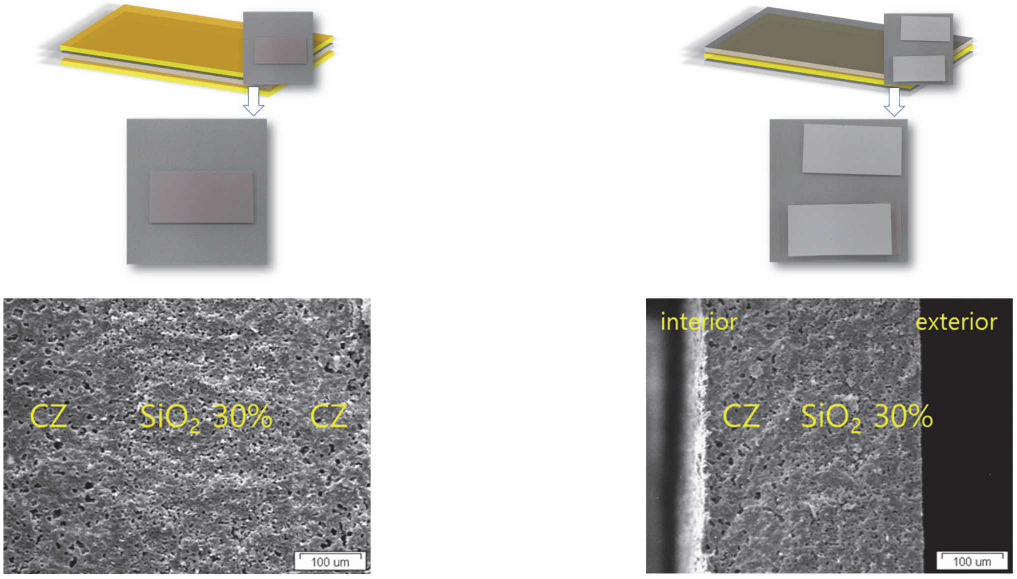
Fig. 6. Various results of sintered hetero laminates.



	x	y	z
SiO_2 30%	13.3%	13.3%	16.5%
SiO_2 50%	1.9%	1.8%	4.1%
CZ 50%	15.3%	15.4%	19.7%
CZ 50% + SiO_2 30% + CZ 50%	15.0%	13.8%	17.8%
SiO_2 30% + CZ 50% + SiO_2 30%	14.2%	13.2%	18.2%

Fig. 7. Shrinkage comparison (among single sheets and hetero laminates).

zirconate 50 vol% is on top (a) and at the bottom (b). As seen in (g) of 'calcium zirconate 50 vol%-silica 50 vol%-calcium zirconate 50 vol%', it is thought that the appearance of all four edges being rolled up is expected when a strong shrinkage amount existed. Strong shrinkage stress along one direction from calcium zirconate 50 vol% (a) is thought to have made curling in the long direction. But when this side faced the floor as in (b), the weaker shrinkage stress along another direction is thought to have made curling in the short direction, while the large deformation from the strong shrinkage stress was suppressed by the self-load. Specimens in (c) and (d) were thought to be fragmented due to the significant difference in shrinkage. Complete bonding occurred by constrained sintering [6] in (e) of 'calcium zirconate 50 vol%–silica 30 vol%–calcium zirconate 50 vol%'. A specimen was separated into two parts with symmetrical thicknesses as shown in (f) of 'silica 50 vol%–calcium zirconate 50 vol%–silica 50 vol%'. Cracks in the central region are thought to have occurred due



(a) CZ 50% + SiO_2 30% + CZ 50%

(b) SiO_2 30% + CZ 50% + SiO_2 30% (separated)

Fig. 8. SEM photos showing interfaces in the hetero laminates.

to the difference in the coefficients of thermal expansion during cooling after the sintering process though the shape was maintained by constrained sintering in (h) of ‘silica 30 vol%–calcium zirconate 50 vol%–silica 30 vol%’.

Figure 7 shows the shrinkage measured by dimensions before and after sintering. In tape casting, it is known that the z-axis shrinkage is large [7,8], but the exceptionally low shrinkage of silica 50 vol% is thought to indicate incomplete sintering, as shown in Fig. 5(b). This phenomenon is thought to have appeared as fragmentation in Figs. 6(c) and (d). And the differences in the shrinkage amounts between the x-axes and y-axes seen in ‘C5+S3+C5’ and ‘S3+C5+S3’ are thought to be related to the directional curling phenomena [shown in Figs. 6(a) and (b)]. This difference is thought to be associated with the orientation of the particles during the tape-casting process [8].

Figure 8 shows scanning electron microscope photos of the junction interface between calcium zirconate 50 vol% and silica 30 vol%, which showed a complete junction. No channel cracks or debonding cracks [6] were observed, although the boundary between heterogeneous LTCCs is apparent clearly. Although the sinterability of each LTCC needs to be improved through several ways such as controlling particle size distributions of glass and fillers, the use of glass in common is thought to be feasible for heterojunction.

4. SUMMARY

The heterojunction of LTCCs with different fillers was investigated by using glass in common. For the LTCC of silica filler with a low dielectric constant and that of calcium zirconate filler with a relatively high dielectric constant, the shrinkage amount was examined through thermomechanical analysis, and the predicted appropriate fraction of each filler was fabricated into green sheets by tape casting. The green sheets of different fillers were alternatively laminated to a thickness of 500 ㎛. As a result of examining the junction, it was observed through SEM that complete bonding was achieved by constrained sintering in the structure of ‘calcium zirconate 50 vol%–silica 30 vol%–calcium zirconate 50 vol%’.

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