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Middle- and high-permittivity dielectric compositions for low-temperature co-fired ceramics

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Abstract

Various middle- and high-permittivity dielectric material systems for LTCC were examined. By designing several borosilicate glass frit systems carefully, we tried to lower the temperature of densification to 875 °C in selected host dielectric materials still maintaining acceptable dielectric properties. The effects of glass addition on the densification, electrical properties, and phase changes in the host dielectric materials were examined.

Keyword: LTCC; Sintering; Dielectric properties; Glass ceramics

1. Introduction

Low-temperature co-fired ceramics (LTCC) technology has become essential in the development of various multifunctional modules and substrates, especially in wireless and/or high frequency applications.[1–3] It is important to incorporate passive components such as resistors, capacitors, inductors, and other functional parts in LTCC multilayer structures in order to achieve highly integrated and multi-functional LTCC modules.[1,4,5] Among the components which could be realized inside the LTCC packages, the resonators and the internal capacitors are most desirable in the current state of the art technology. The resonator structures, which are typical and/or important, consist of planar antenna and filters. Considering the RF frequency range in the current telecommunication system (1–30 GHz) and the typical chip sizes in the packaging technologies (2–10 mm), the most appropriate permittivity (K) range of the materials is 20–100 to realize strip or microstrip resonator structures in LTCC multilayer structures.[6] Meanwhile, the internal capacitors are typically used to realize decoupling capacitors monolithically in the LTCC package. As for the capacitor applications, the high-K dielectric materials are desirable as long as their losses are within an acceptable range.

There have been several approaches to develop the middle-K (K = 20–100) and high-K (K > 500) dielectric material systems which could be fired at below 900 °C. Although some middle-K dielectric compositions have been reported to exhibit the low densification temperature without any additives,[7–9] it is more general and is considered an easy method to add glass frits into the host dielectric compositions to realize the acceptable densification at the low-temperature range of below 900 °C together with good electrical properties.[10–13] The several microwave dielectric compositions including (Zr,Sn)TiO_4,[12] BaO–TiO_2–WO_3,[13] and BaO–Re_2O_3–TiO_2 (Re: La, Sm, Nd, Eu) systems[14,15] have been studied for the development of the middle-k dielectric compositions for LTCC by using glass frits. For examples, Takada et al.[12] reported that (Zr,Sn)TiO_4 ceramic with reactive ZnO–B_2O_3–SiO_2 glass with 5 wt.% was sintered at 1100 °C and had k = 20 and Q = 2100 at a frequency of 8 GHz. Cheng et al.[14] reported that Ba–Nd–Sm–Bi–Ti–O ceramic was sintered at 950 °C by using the BaO–B_2O_3–SiO_2 glass with 5 wt.% and had k = 40 and $Q \times f \sim$ 3000 GHz. However, the temperature of densification was higher than 900 °C, which is still far too high for cofiring of Ag inner electrode.

In this work, we aimed at developing some middle- and high-K dielectric material systems for LTCC by mixing the host dielectric material systems and borosilicate glass frit systems which were carefully designed. We controlled the glass composition and processing parameters so as to lower the densification temperature to 875 °C, while still maintaining acceptable dielec-

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tric properties. The effects of glass addition on the densification and electrical properties were examined.

2. Experimental procedure

The glass compositions were designed with a glass simulation software (SciGlass V3.5, Scivision, USA) in consideration of physical and electrical properties. The designed glass compositions were then fabricated by a conventional glass fabrication process. Powders of SiO_2, B_2O_3, Li_2O, CaO, and Al_2O_3 were used as starting materials for glass fabrication. Through the melting of starting powders in a Pt crucible at the temperatures of 1100–1300 °C and the quenching with a quench roller, glass flakes were prepared. After the ball-milling of the flakes, the average particle size of the glass powders was about 1 μm. The physical and electrical properties of the glass frits were measured from the glass ingots quenched, as summarized in Table 1.

We selected some host dielectric materials which have been reported to exhibit good dielectric properties enough to be applied for LTCC material systems.[7–15] They may be categorized as $K=20$–100 and $K>500$. The detailed compositions, together with their sintering and dielectric properties which are measured from our preliminary studies, are summarized in Table 2. The dielectric compositions were fabricated by a solid state sintering process from the oxide forms of reagents (BaO, TiO_2, ZnO, MgO, ZrO_2, Nb_2O_5, CaO, PbO. All >99.9%, High Purity Chem.). Some of the compositions were the formulated powders from the commercial supplier. In our preliminary experiments, all the dielectric compositions could be densified at temperatures higher than 1300 °C and exhibit the relative density of more than 98% with good dielectric properties, without the addition of glass, as shown in Table 2.

For low-temperature sintering, the host dielectric compositions and 3–25 wt.% of glass frit were mixed by ball-milling for 24 h. The slurry was dried at 90 °C for several hours and granulated with 3 wt.% of a PVA (poly-vinyl alcohol) solution.

Table 1
The physical and electrical properties of the glass frit series developed in this study

	MA series (mol%)	MB series (mol%)	HA series (mol%)
Chemical composition			
LiO_2	33–51	7–50	45–61
B_2O_3	23–43	18–30	30–49
SiO_2	10–35	12–47	5–15
$CaO + AbO_3$	–	2–10	–
Physical properties			
Density (g/cm^3)	2.23–2.68	2.31–2.52	2.35–2.52
$\alpha_{RT-400\,°C}$ ($\times 10^{-6}$ C^{-1})	8.3–14.3	6.3–12.5	10.1–15.3
Glass transition point, T_g (°C)	420–503	371–575	408–450
Glass softening point, T_s (°C)	437–524	390–627	450–480
Dielectric properties			
Permittivity[a]	6.5–8.5	7.0–9.0	7.5–9.5
$Q \times f$ (GHz)[a]	1000–1600	1200–2300	1200–1900
τ_f (ppm/°C)[a]	−80 to −160	−83 to −223	−103 to −153
Tan d (%)[b]	0.4–0.6	0.2–0.5	0.6–0.9

[a] Dielectric properties were measured using a network analyzer in the frequency range of 12–16 GHz.
[b] Tan d were measured using an impedance/gain-phase analyzer at 1 MHz.

The granulated powders were pressed isostatically into pellets at 100 MPa and sintered in the temperature range of 800–950 °C for 2 h in order to evaluate densification behavior.

Microwave dielectric properties were measured by two kinds of methods, viz. the parallel plate resonator method and the cavity resonator method in conjunction with a network analyzer (8720C, HP, USA) in the s_{21} transmission mode examined with a certain frequencies ranging from 8 to 12 GHz. Measurement of dielectric constants mainly hinges on the Hakki–Coleman method with a silver plate followed by an employment of the TE_{011} resonance mode.[16] Unloaded Q values were calculated

Table 2
The physical and electrical properties of the host dielectric materials used in this study

Permittivity range	Abbreviation	Malarial	Sintering properties			Dielectric properties		
			Optimum sintering temperature (°C)	Relative density (%)	Linear shrinkage (%)	Permittivity	$Q \times f$ (GHz)	τ_f (ppm/°C)
Middle-k ($20<k<100$)	MCT	(Mg, Ca)TiO_3	1350	98.7	15.7	21.6	45000	−3
	CZ	$CaZrO_3$	1500	99.5	15.8	28.5	14000	−20
	ZST	(Zr,Sn)TiO_4	1350	99.2	16.1	38.1	52000	−11
	BT4[a]	$BaTi_4O_9$	1350	98.7	16.9	38.6	44500	+3
	B5N4	$Ba_5Nb_4O_{15}$	1375	98.9	15.3	41.5	25000	+68
	BBNT[b]	BaO–Bi_2O_3–Nd_2O_3–TiO_2	1300	98 8	16.3	91.2	6100	+6
	BPNT	$(Ba_{0.5}Pb_{0.5})O\cdot Nd_2O_3\cdot 5TiO_2$	1300	99.5	15.8	94.7	5600	+8
High-k ($k>500$)	BT[c]	$BaTiO_3$	1350	99.8	15.8	>2000[e]	1.9%[f]	–
	BCTZ[d]	$(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$	1260	99.7	16.5	>3000[e]	2.5%[f]	–

[a] Commercial powder (MWF-38, Hayashi Chemical Industry, Co. Ltd., Japan).
[b] Commercial powder (MBRT-90, Fuji Titanium Industry, Co. Ltd., Japan).
[c] Commercial powder (Ferro, Co. Ltd., USA).
[d] Samsung electro-mechanics provided for scientific purposes (not commercial).
[e] Permittivity was measured using an impedance/gain-phase analyzer at MHz.
[f] Tan d was measured using an impedance/gain-phase analyzer at MHz.