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Decreasing of $CaZrO_3$ sintering temperature with glass frit addition

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Abstract

The effects of a glass frit on the sintering and dielectric properties of $CaZrO_3$ ceramics were investigated. The glass frit, which consists of MnO_2, $CaCO_3$, $MgCO_3$, Al_2O_3 and SiO_2, was selected since liquid phase sintering lower the $CaZrO_3$ sintering temperature. The dielectric properties of $CaZrO_3$ with glass frit addition are strongly dependent on the densification. $CaZrO_3$ with glass frit addition can be sintered under 1300 °C (below the nickel's melting point; 1453 °C) and 96% of the theoretical density can be achieved. The dielectric properties at 1MHz are $\varepsilon_r \approx 27$ and a dissipation factor below 0.1%.

Keywords: Glass frit; Low temperature sintering; $CaZrO_3$

1. Introduction

The multilayer ceramic capacitors' (MLCCs) market has been growing in pace with the development of communication technologies [1]. $CaZrO_3$ is an interesting material for both mechanical and electrical applications, such as fuel cells [2], filler [3], resonator [4] for microwave telecommunication and temperature compensating materials of capacitance in MLCC. In temperature compensating dielectrics, there are three classes of RH (-220 ± 60 ppm/°C), TH (-470 ± 60 ppm/°C), UJ (-750 ± 120 ppm/°C) based on a temperature coefficient of capacitance (TCC). $CaZrO_3$ displays a high dielectric permitivity (around 30), low dissipation factor, TCC of 40 [5] and a good behavior under electrical field versus temperature. Through chemical additions, it is suitably formulated to control the TCC and degradation resistance [6]. These properties allow its use in NPO (Negative-Positive Zero) type MLCCs. Almost half of these MLCCs is based on precious metal internal electrodes, such as Pt, Pd and Ag. To reduce the cost of MLCCs while maintaining device performance, precious metal internal electrodes are replaced with base metal electrodes. The best candidate for such a replacement is found to be nickel [7–9]. It is necessary to co-fire the Ni electrodes and $CaZrO_3$ dielectrics in reducing atmospheres to avoid oxidation of the electrode. Also, Ni electrodes have low melting points (1453 °C) that require a decrease in the sintering temperature of the dielectrics.

The purpose of present work is to discuss the lowering of the sintering temperature of $CaZrO_3$ ceramics using a new sintering agent based upon MnO_2, $CaCO_3$, $MgCO_3$, Al_2O_3 and SiO_2 to place this material in an industrial process and its usability as dielectric material in MLCCs with Ni electrodes. Also, the effect of glass frit on dielectric properties of $CaZrO_3$ was investigated.

2. Experimental procedure

Experimental procedure consists of the three parts; preparation of glass frits, synthesis and evaluation of the dielectrics with glass frits addition.

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Table 1
Melting point and compositions of glass frit

Name	Melting point (°C)	Composition
MSA	1140	MnO_2, Al_2O_3, SiO_2
MST	1120	MnO_2, SiO_2, TiO_2
CMAS	1236	$CaCO_3$, $MgCO_3$, Al_2O_3, SiO_2
CAST	1242	$CaCO_3$, Al_2O_3, SiO_2, TiO_2
CMMAS	1220	$CaCO_3$, MnO_2, $MgCO_3$, Al_2O_3, SiO_2
BSS	1210	$BaCO_3$, $SrCO_3$, SiO_2
CMAS2	1255	$CaCO_3$, $MgCO_3$, Al_2O3, SiO_2

2.1. Preparation of glass frits

A glass composition (MnO_2, Al_2O_3, $CaCO_3$, $MgCO_3$, TiO_2, ZrO_2, $SrCO_3$ and $BaCO_3$), which has the lowest melting point in the phase diagram, was chosen as shown in Table 1. These glass compositions were mixed by ball milling, using a zirconia ball and deionized water in a polyethylene pot for 24 h. After ball milling, the mixtures were dried in an oven at 110 °C and melted at 1400 °C for 2 h in a Pt crucible and then quenched into water. The quenched glass was crushed using the planetary mill with a zirconia pot and ball for 5 h and then dried. The mean diameter of the crushed glass frits were 2.98–4.41 μm.

2.2. Synthesis of the dielectrics

$CaZrO_3$ and the glass frit mixed together using a polyethylene pot and zircona balls for 24 h. These mixtures were dried at 110 °C and pressed to a disc of Ø 13 mm × 2 mm under 4.905 × 10 MPa uniaxially. The green disc was heated to 1250–1500 °C with a heating rate of 3 °C/min, soaked for 2 h and cooled to room temperature with a cooling rate of 3 °C/min. In–Ga was attached to the surface of the sintered body as an external electrode to measure its electrical properties.

2.3. Evaluation of the dielectrics

Density was calculated from the volume and weight of the sintered body. The dielectrics constant and dissipation factor were measured at 1 MHz using an Impedance-Gain Phase Analyzer (HP4194A) at a temperature range of −50–130 °C. IR was measured using a High Resistance Meter (HP4339B) at room temperature. The crystal phase and microstructure were analyzed with X-ray diffraction meter (XRD) and scanning electron microscope (SEM), respectively.

3. Results and discussion

Each glass frit was added to $CaZrO_3$ to determine the suitable composition of glass for sintering. Density changes with the sintering temperature of 1250–1650 °C are shown in Fig. 1. The density of the glass frit-free specimen reached its maximum at 1650 °C. The specimen with addition of

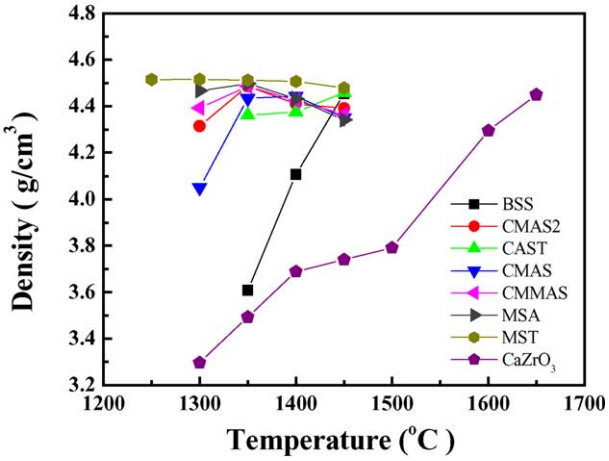

Fig. 1. Density changes of $CaZrO_3$ and $CaZrO_3$–glass frit with increasing temperature.

5 wt.% glass frit lowered the sintering temperature to 200–350 °C compared to that of glass frit-free. It is considered that the addition of glass frit wetted the crystalline grain and accelerated densification. Therefore, the sintered specimen has beyond 97% of relative density at 1300 °C.

Figs. 2 and 3 shows the temperature dependence of the relative dielectric constant of $CaZrO_3$ and $CaZrO_3$ with addition of each glass frits and dissipation factor of $CaZrO_3$ and $CaZrO_3$ with addition of 5 wt.% glass frit sintered at 1300–1350 °C, respectively. $CaZrO_3$ has a dielectric constant and temperature coefficient of 29.5 and 120 ppm/°C. $CaZrO_3$–BSS has 29.4 and 41 ppm/°C, $CaZrO_3$–MSA has 28.8 and 127 ppm/°C, $CaZrO_3$–MST has 28.5 and 105 ppm/°C, $CaZrO_3$–CMAS2 has 27.0 and 38 ppm/°C, $CaZrO_3$–

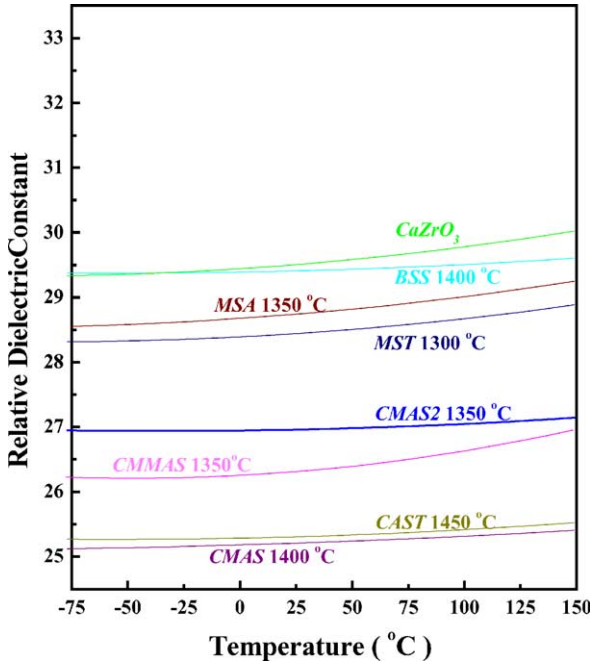

Fig. 2. Relative dielectric constant of $CaZrO_3$ and $CaZrO_3$–glass frit at 1 MHz.

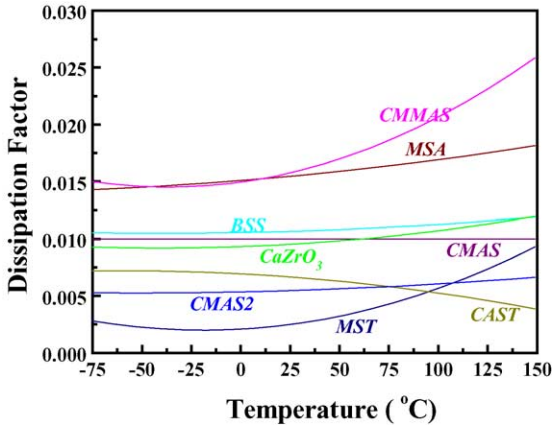

Fig. 3. Dissipation factor of $CaZrO_3$ and $CaZrO_3$–glass frit at 1 MHz.

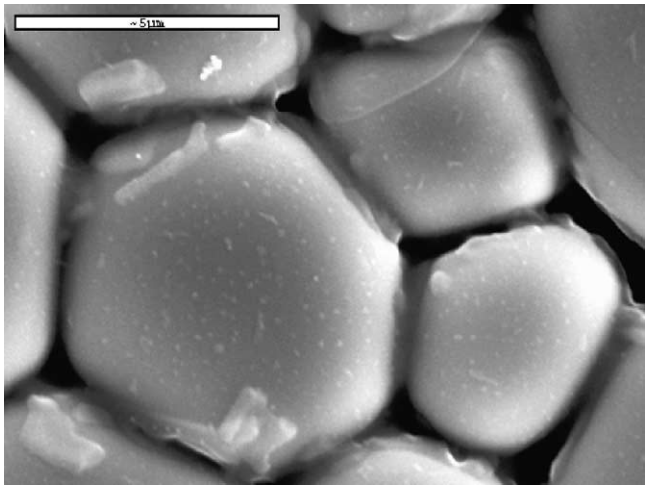

Fig. 4. Microstructure of $CaZrO_3$ with CMAS2 glass frit sintered at 1350 °C. Glass frit was well wetted into crystalline grain.

CMMAS has 26.4 and 145 ppm/°C, $CaZrO_3$–CAST has 25.3 and 52 ppm/°C and $CaZrO_3$–CMAS has 25.2 and 58 ppm/°C, respectively. Dissipation factors are also changed with glass frit. The difference between $CaZrO_3$ and $CaZrO_3$ with glass added dielectric constant is due to the crystal phases and the microstructure composed of the grains wetted by glass with a low dielectric constant. Even though the grain boundary layer of the glass was thin, these microstructures could lower the dielectric constant severely [10]. The scanning electron microscope image of fracture surface of $CaZrO_3$ with CMAS2 glass frit is shown in Fig. 4. $CaZrO_3$ grains were coated by CMAS2 glass frit. It is evidence that glass frit was well-wetted into crystalline grain and accelerated densification. The obtained results from this study summarized in Table 2. The $CaZrO_3$ with 5 wt.% glass frit could be sintered about 1300 °C. The dielectric constant decreased from 29.5 to 25.2 with changing glass frit. Some TCCs of the specimen in this experiment has stable value within large temperature range. Dissipation factor in this system showed under 0.1% (CMAS2, CAST and MST) and resistance above 10^{13} Ω cm.

Table 2
Dielectric properties and sintering temperature of $CaZrO_3$ and $CaZrO_3$–glass frit

Name	Sintering temperature (°C)	TCC (−55 ∼ +125 °C) (ppm/°C)	Dissipation factor[a]	Dielectric constant[a]
$CaZrO_3$	1650	120	0.009	29.5
$CaZrO_3$–MSA	1350	127	0.0154	28.8
$CaZrO_3$–MST	1300	105	0.0017	28.5
$CaZrO_3$–CMAS	1400	58	0.0133	25.2
$CaZrO_3$–CAST	1450	52	0.0058	25.3
$CaZrO_3$–CMMAS	1350	145	0.0155	26.4
$CaZrO_3$–BSS	1400	41	0.0101	29.4
$CaZrO_3$–CMAS2	1350	38	0.0047	27

[a] Room temperature, 1 MHz.

The glass frit was very effective to lower sintering temperature with small amount of 5 wt.%. This approach provides a strong possibility for the manufacture of MLCC in batch process. Furthermore, with chemical addition, it can be use in temperature compensation MLCCs, such as RH, TH and UJ classes.

4. Conclusion

The effect of glass frit on dielectric properties and sinterability of $CaZrO_3$–glass frit system has been investigated to develop the MLCC with Ni internal electrode. The results obtained from this experiment as follows. Addition of 5 wt.% glass frit to $CaZrO_3$ lowered 200–350 °C of sintering temperature. Dielectric constant decreased from 29.5 to 25.2 depend on glasses. Glass frit of CMAS2, CAST and MST added $CaZrO_3$ has a low dissipation factor (under 0.1%).

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