

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 $\epsilon_r \approx 27$ and a dissipation factor below 0.1%.

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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 ($-220 \pm 60 \text{ ppm/}^\circ\text{C}$), TH ($-470 \pm 60 \text{ ppm/}^\circ\text{C}$), UJ ($-750 \pm 120 \text{ ppm/}^\circ\text{C}$) based on a temperature coefficient of capacitance (TCC). CaZrO_3 displays a high dielectric permittivity (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 ₂ O ₃ , SiO ₂
MST	1120	MnO ₂ , SiO ₂ , TiO ₂
CMAS	1236	CaCO ₃ , MgCO ₃ , Al ₂ O ₃ , SiO ₂
CAST	1242	CaCO ₃ , Al ₂ O ₃ , SiO ₂ , TiO ₂
CMMAS	1220	CaCO ₃ , MnO ₂ , MgCO ₃ , Al ₂ O ₃ , SiO ₂
BSS	1210	BaCO ₃ , SrCO ₃ , SiO ₂
CMAS2	1255	CaCO ₃ , MgCO ₃ , Al ₂ O ₃ , SiO ₂

2.1. Preparation of glass frits

A glass composition (MnO₂, Al₂O₃, CaCO₃, MgCO₃, TiO₂, ZrO₂, SrCO₃ and BaCO₃), 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

CaZrO₃ and the glass frit mixed together using a polyethylene pot and zirconia 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 CaZrO₃ 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

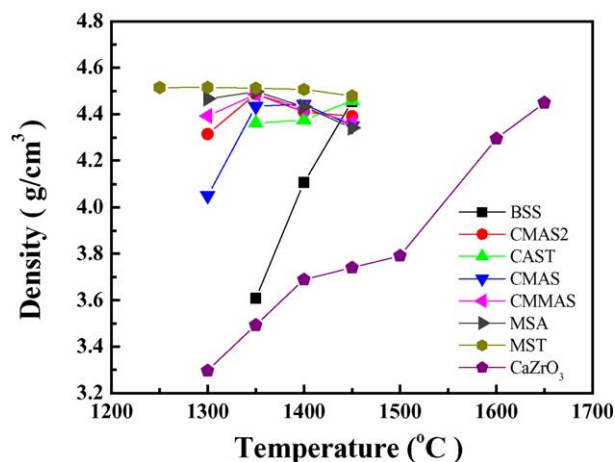


Fig. 1. Density changes of CaZrO₃ and CaZrO₃–glass frit with increasing temperature.

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 CaZrO₃ and CaZrO₃ with addition of each glass frits and dissipation factor of CaZrO₃ and CaZrO₃ with addition of 5 wt.% glass frit sintered at 1300–1350 °C, respectively. CaZrO₃ has a dielectric constant and temperature coefficient of 29.5 and 120 ppm/°C. CaZrO₃–BSS has 29.4 and 41 ppm/°C, CaZrO₃–MSA has 28.8 and 127 ppm/°C, CaZrO₃–MST has 28.5 and 105 ppm/°C, CaZrO₃–CMAS2 has 27.0 and 38 ppm/°C, CaZrO₃–

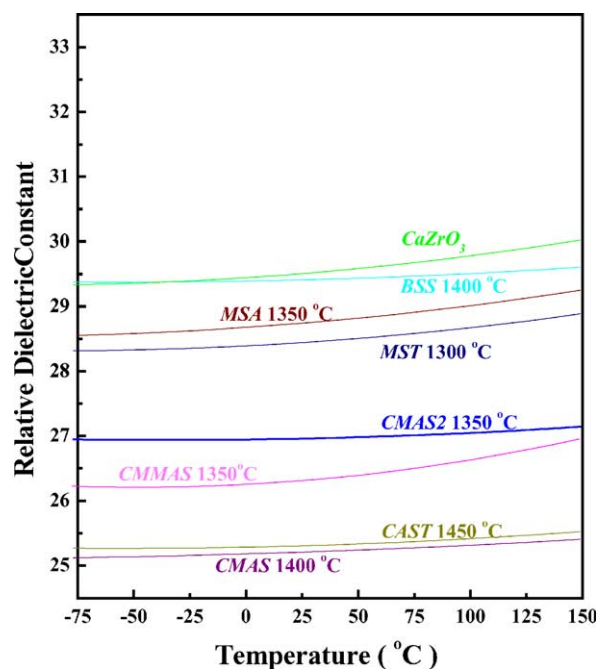


Fig. 2. Relative dielectric constant of CaZrO₃ and CaZrO₃–glass frit at 1 MHz.

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