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Fabrication and performance of dielectric tape based on $CaO-B_2O_3-SiO_2$ glass/Al_2O_3 for LTCC applications

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ABSTRACT

A non-aqueous tape-casting process for fabricating $CaO-B_2O_3-SiO_2$ glass/Al_2O_3 dielectric tape for LTCC applications was investigated. An isopropanol/ethanol/xylene ternary solvent-based slurry was developed by using castor oil, poly(vinyl butyral), and dibutyl phthalate as dispersant, binder, and plasticizer, respectively. The effects of dispersant concentration, binder content, plasticizer/binder ratio, and solid loading, on the properties of the casting slurry and resultant tape were systematically investigated. The results showed that the optimal values for the dispersant and binder contents, plasticizer/binder ratio, and solid loading were 2.0 wt%, 7.5 wt%, 0.6, and 62 wt%, respectively. The resultant flexible and uniform, 120-µm-thick $CaO-B_2O_3-SiO_2$ glass/Al_2O_3 tape had a density of 1.90 g/cm^{-3}, tensile strength of 1.66 MPa, and average surface roughness of 310 nm. Laminated tapes sintered at 875 °C for 15 min exhibited excellent properties: relative density of 97.3%, ε_r of 7.98, tan δ of 1.3×10^{-3} (10 MHz), flexural strength of 205 MPa, and thermal expansion coefficient of 5.47 ppm/°C. The material demonstrated good chemical compatibility with Ag electrodes, indicating a significant potential in LTCC applications.

1. Introduction

Rapid development of wireless communications and microelectronics industries has led to an increase in the demand for miniaturized and integrated electronic devices with high processing speeds [1–3]. Low temperature co-fired ceramic (LTCC) technology with glass-ceramic or glass/ceramic material has been demonstrated as capable of meeting the stringent requirements of electronic devices, owing to its outstanding dielectric, thermal, and mechanical properties, and the ability to be co-fired with high-conductivity electrodes such as Cu, Ag and Au, below 900 °C [4]. Among the different LTCC material systems, borosilicate glass/Al_2O_3 composite has been reported to be particularly suited for use in microelectronic packaging, mainly due to its good dielectric properties and high mechanical strength [5,6]. There has been considerable research on the development of the $CaO-B_2O_3-SiO_2$ (CBS) glass/Al_2O_3 LTCC material system [7,8]. However, after the development of LTCC material systems, the fabrication of high-performance LTCC green tapes becomes a critical technological issue for practical applications.

Tape casting, a well-established and low-cost technique, is extensively used for the fabrication of large-area thin and flat ceramic sheets, primarily for applications such as multilayer capacitors, highly integrated circuits, and solid oxide fuel cells [9–11]. The key to this process lies in the preparation of a well dispersed and stable deflocculated slurry of ceramic powder in a non-aqueous or aqueous solvent system with the aid of dispersants, binders, plasticizers, and other additives. The resultant slurry is cast onto a stationary or moving surface by evaporating the solvent. As a result, a dried green tape is left behind, which must be stripped from the surface of the carrier film and cut into appropriate shapes. Generally, the amount and type of organic components in a casting slurry system should be adjusted to fit each given ceramic powder in order to obtain a high-performance green tape. In recent years, there have been numerous literature reports on the composition and properties of tape-casting slurries and characteristics of the resultant green tapes. Mukherjee [12] investigated the role of the dispersant and powder size on slurry rheology, and the corresponding effect on green as well as sintered densities of tape-cast yttria-stabilized zirconia. Ceylan [13] explored the role of organic additives in non-aqueous tape casting of SiAlON ceramics. However, there have been no reports on a comprehensive and systematic investigation on the relationship between the casting-slurry composition and the resultant tape.

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In the present work, we have developed a non-aqueous tape-casting process for fabricating $CaO-B_2O_3-SiO_2$ glass/Al_2O_3 dielectric tape for LTCC applications. An isopropanol/ethanol/xylene ternary solvent-based slurry was prepared by employing castor oil, poly(vinyl butyral), and dibutyl phthalate as a dispersant, binder and plasticizer, respectively. The effects of the dispersant and binder content, plasticizer/binder ratio, and solid loading on the properties of the casting slurry and resultant green tape were systematically investigated. In addition, the sintering densification, crystalline-phase composition, dielectric characteristics, thermal and mechanical properties, and co-firing behavior with Ag electrodes of the sintered $CaO-B_2O_3-SiO_2$ glass/Al_2O_3 LTCC material were investigated.

2. Experimental procedure

$CaO-B_2O_3-SiO_2$ (CBS) glass with a composition of 63 wt% SiO_2, 14 wt% B_2O_3, 12 wt% CaO, 5 wt% Al_2O_3, 1.8 wt% MgO, 2.6 wt% Na_2O, and 1.6 wt% K_2O, was synthesized through the melting and quenching route. The glass synthesis began with the selection of high-purity (≥ 99.5%) SiO_2, H_3BO_3, $CaCO_3$, Al_2O_3, $MgCO_3$, Na_2CO_3, and K_2CO_3 as raw materials. Then, the well-mixed raw-material powder was melted in a platinum crucible at 1450 °C for 0.5 h and the resultant glass melt was rapidly quenched in deionized water to form homogenous glass frits. The glass frits were crushed to 0.25 mm using a roller crusher and then ball milled in deionized water for 20 h with zirconia balls. The resulting CBS glass powder was mixed thoroughly with Al_2O_3 powder (mass ratio of 50 wt%:50 wt%) for 24 h. The average particle size and BET surface area of the powder (listed in Table 1) were determined by the laser-diffraction method (MS2000, Malvern, UK) and a surface-area analyzer (Gemini 2375, Micromeritics, USA), respectively.

The tape-casting slurry was prepared by a two-stage process. The first stage was the dispersion of the CBS glass/Al_2O_3 mixed powder in a solvent system in the presence of a dispersant by ball milling for 12 h, and the second involved mixing with the binder and plasticizer and further ball milling for an additional 24 h. In this study, a ternary system of isopropanol (56 wt%, Sinopharm Chemical Reagent Co., Ltd, China), ethanol (31 wt%, [13]idem) and xylene (13 wt%, [13]idem) was used as solvent, and castor oil (Shanghai Lingfeng Chemical Reagent Co., Ltd, China) was used as dispersant. Poly(vinyl butyral) (PVB, B60H, Kuraray, Japan) and dibutyl phthalate (DBP, Shanghai Lingfeng Chemical Reagent Co., Ltd, China) were used as the binder and plasticizer, respectively. The homogenized slurry was vacuum degassed for 15 min and then cast into 120-μm-thick green tapes using a tape-casting machine (BHLY-011A, Guangdong Fenghua Advanced Technology Holding Co., Ltd, China) at a casting speed of 200 mm/min. The green tapes were dried at room temperature in ambient atmosphere. Circular sheets of 18-mm diameter were cut from the dried green tapes. To investigate the co-firing behavior of the green tape and metal electrodes, silver pastes (6148Ag, DuPont, USA) were screen printed layer-by-layer upon the green tape, followed by stacking and lamination (60 layers) under a 21-MPa pressure at 70 °C for 1 h. Finally, after a debinding process at 300 °C for 1 h and 450 °C for 3 h, the laminated sheets were sintered at 875 °C for 15 min (according to our previous work [14], the CBS glass/Al_2O_3 composite sintered at this temperature shows a more compact structure and excellent performance) at a constant heating rate of 5 °C/min.

The shear viscosity of the casting slurry was measured using a rheometer (R/S Plus, Brookfield, USA) and a sedimentation analysis was performed by transferring 10-mL slurry into a graduated measuring cylinder to settle. The updated settling height (*H*) was recorded at regular time intervals, and the ratio of the settling height (*H*) to initial height (H_0, 10 mL) was calculated. The green-tape densities were the average of five samples, calculated using the density formula, i.e., mass divided by volume. The mechanical properties of the tapes and sintered sheets were measured using an electronic universal material testing machine (Model 5566, Instron Co., UK). The thermogravimetric analysis (TG) of the green tape was performed using a thermal analyzer (STA 409 PC/PG, NETZSCH, Germany) at a heating rate of 10 °C/min in the 25–600 °C temperature range. The surface roughness of the green tape was evaluated using an atomic force microscope (AFM, Dimension Edge, Bruker, Germany) operating in the tapping-mode regime. The crystalline phases and micrographs were analyzed by powder X-ray diffraction (XRD, X'TRA, ARL, Switzerland) and scanning electron microscopy (SEM, JSM-5900, JEOL, Japan), respectively. The coefficient of thermal expansion (CTE, 25–300 °C) was measured with a dilatometer (DIL 402EP, Netzsch, Germany) at a heating rate of 5 °C/min in air. The dielectric performance was tested by an impedance analyzer (4284A, Agilent, USA).

Table 1
Characteristics of CBS glass and Al_2O_3 powders.

Powders	Average particle size (μm)	BET surface area ($m^2\,g^{-1}$)
CBS glass	3.5	2.3
Al_2O_3	2.7	1.8

3. Results and discussion

The preparation of a homogeneous and stable tape-casting slurry, with good flowing properties, is important for guaranteeing the quality of the final LTCC tapes. The dispersant content required to keep the ceramic particles deflocculated in the slurry should be a primary consideration. The rheological characteristics of the slurry were investigated to determine the dispersibility of the tape-casting slurry as a function of the castor oil (dispersant) content. Fig. 1 represents the rheological behavior of the CBS glass/Al_2O_3 suspension with an initial powder loading of 68 wt% (with respect to solvent) as a function of the castor oil content (0.5–2.5 wt% of powder weight). The shear viscosities of all slurries decreased exponentially as the shear rate increased from 0 to 200 s^{-1}, exhibiting shear-thinning behavior [15] (also known as pseudoplasticity) that is widely considered to be essential for the tape-casting slurry. The slurry viscosity decreased while passing through the blade gap due to the shear force, and increased immediately after the blade, preventing unwanted flow after casting. It was difficult to avoid the formation of agglomerates in the concentrated suspensions despite the use of dispersants, and the shear-thinning behavior was the consequence of the gradual breaking of these agglomerates under the shear stress [16]. As seen in Fig. 1, as the dispersant concentration increased from 0.5 wt% to 2.0 wt%, the shear viscosity decreased noticeably. However, further increase in the dispersant content from 2.0 wt% to 2.5 wt% resulted in a slight increase in the shear viscosity. Thus, the

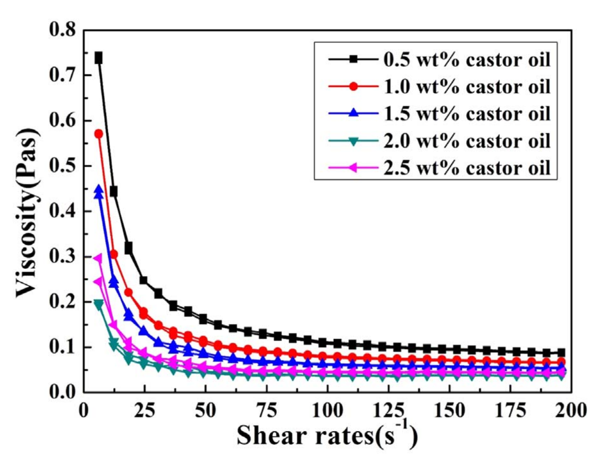

Fig. 1. Rheological behaviors of CBS glass/Al_2O_3 suspension with an initial powder loading of 68 wt% as a function of dispersant content.