Effects of various fillers on sintering, microstructures and properties of Ca-Ba-Al-B-Si-O glass/ceramic composites

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Abstract: Low-temperature sintering and properties of LTCC (low temperature co-fired ceramics) materials based on CaO-BaO-Al\(_2\)O\(_3\)-B\(_2\)O\(_3\)-SiO\(_2\) glass and various fillers such as Al\(_2\)O\(_3\), silica glass, chrisobalite, AlN, ZrO\(_2\), MgO-SiO\(_2\), TiO\(_2\) were investigated. The results show that densification, crystallization, microstructures and dielectric properties of the composites are found to strongly depend on the type of filler. The densification process of glass/ceramic composites with various fillers is mainly from 600 °C to 925 °C, and the initial compacting temperature of samples is 600 °C. The initial rapid densification of samples starts at its glass softening temperature. LTCC compositions containing Al\(_2\)O\(_3\), silica glass, AlN and MgO-SiO\(_2\) fillers start to have the crystallization peaks at 890, 903, 869 and 844 °C, respectively. The crystallization peaks are believed as correlated to the crystallization of Ca\(_4\)Al\(_2\)SiO\(_8\), \(\beta\)-SiO\(_2\), \(\alpha\)-Si\(_2\)Al\(_2\)SiO\(_7\) and \(\beta\)-SiO\(_2\). The composite ceramic with Al\(_2\)O\(_3\), silica glass and TiO\(_2\) ceramic have a better dense structure and better smooth fracture surface. Sample for Al\(_2\)O\(_3\) has the lowest dielectric loss \(\tan \delta\) value of 0.00091, whereas the sample for MgO-SiO\(_2\) has the highest dielectric loss \(\tan \delta\) value of 0.02576. The sample for TiO\(_2\) has the highest dielectric constant value of 14.46, whereas the sample for Al\(_2\)O\(_3\) has the lowest dielectric constant value of 4.61.

Key words: borosilicate glass; softening temperature; filler; microstructures; sintering; dielectric properties

1 Introduction

The development of wireless communication components and modules with high wiring density, high volumetric efficiency, high performance, high level of integration, excellent reliability, and low cost required specially high quality of dielectric materials [1]. LTCC (low temperature co-fired ceramics) with high electrical conductivity metallization such as silver have been identified to be a feasible solution for applications in the area of wireless communications [2–3]. However, the substrate materials with low sintering temperature (lower than 900 °C), proper xy-shrinkage, good dielectric properties and compatibility with Ag electrodes of dielectric materials were necessary in order to achieve the co-fired process of LTCC materials [4–7]. The glass matrix easily enabled low temperature co-fired with low-resistance metals such as silver, glass crystallization was utilized to ensure post-firing stability, and the large variety of utilisable glasses and ceramic fillers in different ratios permitted the continuous tuning of LTCC properties in wide ranges [8]. Most previous studies have been focusing on the development of new glass as a critical factor on determining the final performance of LTCC components and devices. LEE et al [9] reported that 70% 20BaO·15Nd\(_2\)O\(_3\)·35TiO\(_2\)·30B\(_2\)O\(_3\) glass and 30% Al\(_2\)O\(_3\) exhibited \(k \approx 22\) and \(\tan \delta \approx 0.009\) with nearly full densification at 850 °C. LO et al [10] reported that 25CaO–25Al\(_2\)O\(_3\)–50SiO\(_2\) system glass-ceramics with 5% TiO\(_2\) possessed the lowest permittivity of 8 and exhibited appropriate dielectric properties. BaO-Al\(_2\)O\(_3\)-B\(_2\)O\(_3\)-SiO\(_2\) glass could effectively improve the densification of the composites since its lower glass softening temperature (about 700 °C) [11–12]. Moreover, the Al\(_2\)O\(_3\) filler with higher thermal stability, the AlN filler with higher thermal conductivity and some functional fillers (SiO\(_2\), ZrO\(_2\), MgO-SiO\(_2\), TiO\(_2\)) could adjust the dielectric constant and shrinkage of samples was the basic principle of choosing filler...
materials. However, the choice of filler (Al₂O₃, christobalite, silica glass, AlN, ZrO₂, MgO·SiO₂, TiO₂) for preparing different functional ceramics has not been extensively investigated yet.

Low-temperature sintering and dielectric properties of LTCC materials based on a typical CaO-BaO-Al₂O₃-B₂O₃-SiO₂ glass and various fillers such as Al₂O₃, christobalite, silica glass, AlN, ZrO₂, MgO·SiO₂, TiO₂ were investigated. The property changes of composites were expected from the unique characteristics of the filler. A fixed amount of an identical glass based on the common borosilicate glass was used to directly compare the effects of various fillers on densification, crystallization, microstructure and dielectric properties of the composites. The relationships among the sintering temperature, microstructure evolution and properties of glass/ceramic composites with various fillers were also presented.

2 Experimental procedure

10CaO-17BaO-3Al₂O₃-8B₂O₃-58SiO₂-(4(Na₂O+K₂O)) glass and various ceramic powders were used as the raw materials. Reagent-grade CaCO₃, BaCO₃, Al₂O₃, H₃BO₃, SiO₂, Na₂CO₃, and K₂CO₃ were chosen as the raw materials. The constituents were mixed and blended uniformly, and then the glass was prepared with the high temperature melting method at 1400–1500 °C for about 1–20 h. After the last melts were quenched into distilled water, borosilicate glass crushed was acquired. Then the glass frit after drying and crushed was milled using water, borosilicate glass crushed was acquired. Then the glass was 2.86 μm in average, and then followed by sintering at the temperature range from 800 °C to 925 °C for 15 min with a heating rate of 5 °C/min.

The granularity of the powders was measured by NSKC-1 Photo Size using distilled water as media. Glass transition and crystallization temperature of samples were determined by differential scanning calorimeter (DSC) at N₂ atmosphere with a heating rate of 10 °C/min (NETZSCH-STA 449C, α-alumina reference material). For sintering process at the temperature range from 550 °C to 925 °C for 15 min with a setting heating rate of 5 °C/min, the linear shrinkage (in-plane direction for xy direction) of the samples can be measured using micro-calipers, which is obtained by measuring more than 10 points then averaging. The phase composition of the samples was determined by X-ray diffraction with Cu/Kα radiation (λ=0.15405 nm) (XRD ARL X/TRA). The microstructures of cross section of the samples were examined by scanning electron microscopy (SEM JSM-5900). Bulk density and porosity of the fired samples measurements were measured by Archimedian immersion method using water as media with the accuracy of ±0.01 g/cm³. The dielectric properties such as dielectric constant (εᵣ), dielectric loss (tanδ) were measured by Agilent 4294A+16047E impedance analyzer, and the test frequency was 10 MHz. The dielectric constant was calculated by

\[ εᵣ = \frac{144 × h × C}{D × D} \]

where, εᵣ is relative dielectric constant, h is the height of sample, C is the capacity of sample, D is the diameter of sample.

Three-point strength (3dp) of samples was measured by electronic universal tensile testing machine (CMT6208). The value of coefficient of thermal expansion (CTE) was measured by thermal expansion instrument RPZ-01 from room temperature to 500 °C.

3 Results and discussion

3.1 Analysis of raw materials and green tape

Figure 1 shows the XRD patterns of various raw samples. The XRD patterns of samples show their corresponding ceramic crystalline, while silica glass exhibits no crystalline. Relevant characteristic peaks for ceramics are strong, and that demonstrates that the crystallinity of corresponding crystal is good. Figure 2 shows characterization images of glass/Al₂O₃ composites green tape. The glass and Al₂O₃ powders are less than 10 μm, and the green sheet has a dense structure (Fig. 2(a)). The exothermic peaks appearing below