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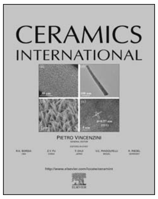

Low-dielectric-constant $LiAlO_2$ ceramics combined with LBSCA glass for LTCC applications

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ABSTRACT

This study used $Li_2O–B_2O_3–SiO_2–CaO–Al_2O_3$ (LBSCA) glass to reduce the sintering temperature of $LiAlO_2$ ceramics and to realise the low dielectric constants ($\varepsilon_r < 5$) of low-temperature co-fired ceramic (LTCC) materials. LBSCA glass remarkably enhanced the densification of $LiAlO_2$ ceramics. X-ray diffraction patterns indicated that only the γ-$LiAlO_2$ phase occurred within the doping range of 1 wt% to 3.5 wt%. Scanning electron microscopy images showed dense and uniform grains in samples with 3.0 wt% LBSCA glass. These samples also exhibited low dielectric constants and low dielectric loss when sintered at 900 °C and 950 °C (i.e., ε_r=4.48, Qf=35,540 GHz and τ_f=−53 ppm/°C at 900 °C; ε_r=4.50, Qf=38,979 GHz and τ_f=−55 ppm/°C at 950 °C, respectively). The material prepared was chemically compatible with silver and showed potential in applications of high-frequency LTCC microwave substrates.

1. Introduction

With the rapid development of wireless communication, an increasing number of studies have focused on materials with excellent microwave dielectric properties. Miniaturisation devices with high integration level can be obtained with multilayer structures [1]. Low-temperature co-fired ceramic (LTCC) technology serves as the best candidate for miniaturisation and integration of microwave devices, circuits and systems. However, co-firing with Ag electrodes requires a reduction of the sintering temperature of substrate materials (Ag melting point: 961 °C) [2,3]. Propagation delay also plays a significant role in signal transmission in substrates. Signal delay time is directly proportional to the square root of dielectric constants, as shown by the formula $t_d = \frac{\sqrt{\varepsilon_r}}{c} l_e$ (where t_d corresponds to signal delay time, l_e represents transmission distance and c stands for velocity of light). Therefore, the development of microwave communication technology at high frequencies demands the use of microwave substrate materials with low dielectric constants. In recent years, numerous studies have been conducted on microwave dielectric ceramic materials, such as Zn_2SiO_4, Mg_2SiO_4 and $CaWO_4$, with low dielectric constants and fired at low temperatures [4–9]. Most of these materials featured dielectric constants greater than 5.7. Some materials had low dielectric constants ($\varepsilon_r < 5$), such as $Li_3AlB_2O_6$, $LiAlSiO_4$+15 wt% Bi_2O_3, $0.8SiO_2–0.2B_2O_3$ [10–12]. However, these materials contained extremely low melting oxide or glass additions, which might make tape casting difficult [13].

Yang reported that the dielectric constant of $LiAlO_2$ equals 4.4, and it conforms to the requirement of low dielectric constants [14]. $LiAlO_2$ is a cutting-edge material extensively used as a ceramic matrix for molten carbonate fuel cells [15]. However, few studies have investigated in detail the microwave dielectric properties of $LiAlO_2$ ceramics and their characteristics under sintering at low temperatures. Manufacturing dense $LiAlO_2$ ceramics requires sintering at temperatures higher than 1400 °C [16]. A proper sintering aid must be adopted to reduce sintering temperatures to 900 °C and to utilise $LiAlO_2$ in LTCC technology. In LTCC materials, sintering aids commonly include low melting glass additions. However, inadequate or excessive glass additions can lead to either high microwave dielectric loss or crack formation during soldering, especially when the amount of glass doping exceeds 5 wt% [17]. Therefore, proper sintering aids should be selected to produce high-performance and low-temperature co-fired $LiAlO_2$ ceramics.

In this study, $Li_2O–B_2O_3–SiO_2–CaO–Al_2O_3$ (LBSCA) glass was used to lower the sintering temperature of $LiAlO_2$ ceramics and to meet the requirements of LTCC application. We investigated the effects of adding LBSCA to the sintering characteristics, microstructure and microwave dielectric properties of ceramics. The chemical compatibility of the $LiAlO_2$ ceramic with Ag was also investigated. We manufactured $LiAlO_2$-based LTCC materials with low dielectric constant and high-quality factor; these materials exhibit potential applications in high-frequency LTCC substrate materials.

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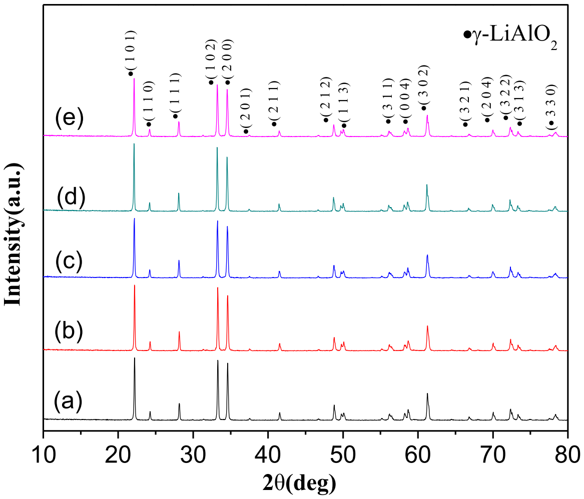

Fig. 1. XRD patterns of $LiAlO_2$ ceramics with *x* wt% LBSCA additive and sintered at 900 °C; (a) *x*=1, (b) *x*=2, (c) *x*=2.5, (d) *x*=3 and (e) *x*=3.5.

2. Experimental procedure

Starting materials comprised high-purity powders of Li_2CO_3 (99%) and Al_2O_3 (99%). Li_2CO_3 and Al_2O_3 were milled at a 1:1 mol ratio in a nylon pot filled with zirconia balls. The materials were then dried and calcined at 950 °C for 3 h to obtain pre-sintering powders. LBSCA glass was prepared by quenching method. Oxide raw materials were mixed and melted at 1000 °C for 2 h in an alumina crucible at a molar ratio of Li_2O:B_2O_3:SiO_2:CaO:Al_2O_3=52.45:31.06:11.99:2.25:2.25 [18]. The solution was then removed from the furnace and poured with cold water to obtain glass materials. Approximately 1.0 wt% to 3.5 wt% of LBSCA glass materials were doped into $LiAlO_2$ pre-sintering powders, and mixtures were milled in nylon pots with zirconia balls for 12 h. The powders were then pressed into cylinders by uniaxial pressing after drying and mixing with polyvinyl alcohol binder. Specimens were finally sintered at 850, 900 and 950 °C for 3 h. The chemical compatibility with Ag was investigated by co-firing the mixed powders with 30 wt% Ag powders in ambient atmosphere at 900 °C for 3 h. Some 3.0 wt% LBSCA glass-doped $LiAlO_2$ ceramic specimens with Ag electrode (EL 43-038) coating were co-fired at 900 °C for 3 h in air.

Phase structures were analysed through X-ray diffraction (XRD: DX-2700) using Cu Kα radiation. Bulk densities of samples were measured using Archimedes' principle. Relative densities were obtained by ratios of bulk and theoretical densities. Sample section micrographs were examined by scanning electron microscopy (SEM: JEOL JSM6490LV). Microwave dielectric properties were measured with the Hakki–Coleman method and Agilent N5230A Network Analyzer. Transmission cavity method was used to determine quality factors. The samples with Ag were analysed through XRD (DX-2700), SEM (JEOL JSM-7600F) and energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

Fig. 1 shows the XRD patterns of $LiAlO_2$ with different amounts of LBSCA glass and sintered at 900 °C. $LiAlO_2$ features three known crystal forms: α-$LiAlO_2$, β-$LiAlO_2$ and γ-$LiAlO_2$ [19]. The figure shows that all of the samples exhibited a pure γ-$LiAlO_2$ phase. Results did not show any peak that can confirm the occurrence of α-$LiAlO_2$ or β-$LiAlO_2$ phases; this observation can be attributed to the transformation of α-$LiAlO_2$ and β-$LiAlO_2$ phases into γ-$LiAlO_2$ at high temperatures [20]. In all of the samples, the positions of diffraction peaks seldom changed, indicating that components of LBSCA glass did not enter $LiAlO_2$ crystal lattices and did not change lattice parameters. LBSCA glass was amorphous at grain boundaries.

Fig. 2 shows SEM micrographs of $LiAlO_2$ with different amounts of LBSCA glass and sintered at 900 °C. The sample with 1.0 wt% LBSCA glass presented intergranular gaps, indicating that it was not dense enough. With the increase of glass content, the average grain size increased slightly and intergranular gaps gradually disappeared. This finding can be attributed to the low-melting-point LBSCA glass that forms a liquid-phase layer and facilitates the so-called liquid-phase sintering process, which is beneficial to the growth of grains and the improvement of densification. However, after incorporating large contents of LBSCA glass at more than 3.0 wt%, the average grain size exhibited a slight decrease. This finding can be attributed to the excessive deposition of glass in grain boundaries, which hinders the growth of the grains.

Tests were conducted on relative densities of $LiAlO_2$ ceramics with different amounts of LBSCA glass and sintered at 850, 900 and 950 °C; results are shown in Fig. 3. Relative density first increased as the LBSCA content increased, regardless of the different sintering temperatures. This phenomenon occurred as LBSCA glass melted (melting temperature of LBSCA glass is 390 °C [21]) before reaching the sintering temperature of $LiAlO_2$; the liquid phase of LBSCA glass efficiently promoted densification, decreased the number of pores and lowered the sintering temperature of sample materials [22]. Thus, LBSCA glass enhanced the densification of $LiAlO_2$ ceramics, coinciding with the results shown by SEM micrographs. Relative densities of 3.0 wt% LBSCA glass peaked when they were sintered at 900 and 950 °C. When the $LiAlO_2$ samples with 3.5 wt% LBSCA glass were sintered at 900 and 950 °C, the relative densities decreased slightly. This finding can be attributed to the fact that excess LBSCA glass hinders grain growth. By contrast, when sintered at 850 °C, the relative densities of samples continuously increased, implying that 3.0 wt% LBSCA glass was insufficient to densify samples sintered at 850 °C but was adequate for those sintered at 900 and 950 °C.

Fig. 4 shows dielectric constants (ε_r) of $LiAlO_2$ with different amounts of LBSCA glass and sintered at different temperatures. Non-densification resulted in low dielectric constant of samples with 1.0 wt % LBSCA glass. As the LBSCA glass content in samples sintered at 850 °C increased, the dielectric constant increased monotonously with density during sintering. When sintered at 900 and 950 °C, the dielectric constants of samples with 3.0 wt% LBSCA glass peaked and then slightly decreased. Remarkably consistent variation was observed in the dielectric constants of samples with different LBSCA glass contents and sintering densities, indicating that the dielectric constant is mainly influenced by changes in density. Samples peaked with dielectric constants of 4.48 and 4.50 when sintered at 900 and 950 °C, respectively. Values meet the requirements of low dielectric constants.

Fig. 5 shows the *Qf* values of $LiAlO_2$ ceramics doped with different LBSCA glass contents and sintered at different temperatures. Microwave dielectric loss includes intrinsic and extrinsic losses, with extrinsic losses playing a more significant role [23,24]. *Qf* values were highly affected by densification and grain uniformity [25,26]. The figure also shows that the *Qf* values first increased and then decreased with increasing LBSCA content under all sintering conditions; such results are mainly due to the density increase before added LBSCA reached 3.0 wt%. Fig. 3 shows that $LiAlO_2$ ceramics were not highly dense when doped with less than 3.0 wt% LBSCA glass and showed