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Crystallization behavior and microwave dielectric properties of low loss $MgO-Al_2O_3-SiO_2-MnO_2-ZnO$ and $MgO-Al_2O_3-SiO_2-GeO_2$ microcrystalline glass-ceramics for LTCC substrate applications

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ABSTRACT

In this study, 21.9 mol% MgO - 20.3 mol% Al_2O_3 - 54.6 mol% SiO_2 + 1.6 mol% MnO_2 + 1.6 mol% ZnO and 23.1 mol% MgO - 20.9 mol% Al_2O_3 - 55.0 mol% SiO_2 + 1.0 mol%GeO_2 were prepared by low-temperature co-firing method. The effects of nucleating agents and sintering temperature on the crystallization behavior, microstructure and microwave dielectric properties of MASMZ and MASG glass-ceramics were investigated. It was found that both glass-ceramics were able to precipitate stable α-cordierite crystalline phases at relatively low temperatures. Crystallization kinetics analysis showed that MASMZ glass-ceramics crystallized more easily than MASG glass-ceramics. MASMZ glass-ceramics exhibited optimal dielectric properties at 925 °C: $\varepsilon_r = 4.74$, $\tan\delta = 8.1 \times 10^{-4}$, $\tau_f = -14$ ppm/°C. MASG glass ceramics achieved optimal dielectric properties at 950 °C: $\varepsilon_r = 4.46$, $\tan\delta = 1.11 \times 10^{-3}$, $\tau_f = -27$ ppm/°C. Especially, the excellent chemical stability and compatibility of MASMZ and MASG glass-ceramics with silver at high temperatures were verified, indicating the potential of MASMZ and MASG glass ceramics as LTCC substrate materials.

1. Introduction

With the rapid progress of modern technology, traditional high-temperature co-fired ceramic technology is no longer sufficient to meet the demands for portability and integration of electronic components. To address the challenge of the miniaturizing electronic components, they need to be embedded inside rather than on the surface, and the selected substrate material must possess excellent electrical insulation properties and be compatible with the physical, chemical, and electromagnetic properties of the internal components. Therefore, the low-temperature co-fired ceramics (LTCC) technology emerged at the right moment [1–3]. Among various substrate materials, glass-ceramics have attracted significant attention due to their excellent dielectric properties and adjustable thermal expansion coefficients. Cordierite glass-ceramics, in particular, stand out for their low relative permittivity (ε_r), low dielectric loss (tanδ), and low thermal expansion coefficients, making them ideal LTCC substrate materials [4–8]. However, their high sintering temperature limits their application in the LTCC field. Adding crystal nucleating agents during the glass preparation stage has become a key research direction in the development of cordierite glass-ceramics [9–14].

For instance, Liu et al. studied the evolution of phases, microstructure, luminescence, and mechanical properties of $MgO-Al_2O_3-SiO_2$-based glass-ceramics doped with Cr_2O_3 [15]. Luo et al. [16] investigated the formation of α-cordierite glass-ceramics in $MgO-Al_2O_3-SiO_2$ systems with and without the addition of B_2O_3, finding that an appropriate

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