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A novel phase-controlling-sintering route for improvement of diopside-based microwave dielectric materials

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Abstract

The present work suggests a new reactive route for obtaining $MgTiO_3$-doped $CaMgSi_2O_6$ glass–ceramic microwave dielectric material with very low dielectric constant (ε_r), high quality factors ($Q \times f$) and nearly zero temperature coefficient of resonant frequency (τ_f). Sintering of the mixture of $CaMgSi_2O_6$ glass and synthesized $MgTiO_3$ powders at 950 °C results in glass-ceramics containing Mg_2SiO_4 and $CaTiO_3$ phases. Such glass-ceramics possess increased quality factors and improved temperature coefficient of resonant frequency, because the Mg_2SiO_4 and $CaTiO_3$ phases own ultra-high $Q \times f$ and positive τ_f, respectively. Microstructure features and EPMA line scan show the concentration gradients of Ca, and Si atoms altering from matrix region toward $MgTiO_3$ particle. These data indicate that during the liquid phase sintering silica glass reacts with $MgTiO_3$ ceramic particles forming the Mg_2SiO_4 and $CaTiO_3$ phases.

Keywords: Diopside; Glass–ceramic; Microwave dielectrics

1. Introduction

The telecommunication and satellite broadcasting industry has created a high demand for microwave ceramic components. In particular microwave substrate materials with a very low dielectric constant (ε_r) to reduce the RC delay time of electronic signal [1,2], a very high quality factor ($Q \times f$) to achieve high selectivity and nearly zero temperature coefficient of resonant frequency (τ_f) for frequency stability are of great interest. Several low ε_r and high $Q \times f$ ceramics systems have been developed over the years. For example, Song and Chen [3] mentioned that forsterite (Mg_2SiO_4) possesses a low ε_r of 6.8, an ultra-high $Q \times f$ of 270,000 GHz and diopside ($CaMgSi_2O_6$) ceramics demonstrate optimum dielectric properties: $\varepsilon_r = 7.46$, $Q \times f = 59{,}700$ GHz. However, both these materials show large τ_f values of -73 ppm/°C and -42.3 ppm/°C respectively. In order to achieve the nearly zero τ_f, the diopside and Mg_2SiO_4 ceramics were added with compositions owning high positive τ_f to compensate the τ_f value. Namely $CaTiO_3$ ($\varepsilon_r = 170$, $Q \times f = 3600$ GHz, $\tau_f = +800$ ppm/°C) [4] was added to diopside and Mg_2SiO_4 ceramic was added with TiO_2 ($\varepsilon_r = 104$, $\tau_f = +400$ ppm/°C) [5]. Such doping indeed improved the τ_f values. However, the quality factors decreased because of the low $Q \times f$ values of $CaTiO_3$ and TiO_2 phases. Besides, these materials do not meet the requirement of microwave dielectric components for low temperature co-fired ceramics (LTCC) process because of their high sintering temperatures (> 1300 °C). Development of glass ceramic systems seems to be a possible way to reduce the sintering temperature to the values compatible with the LTCC process while maintaining the outstanding dielectric properties.

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For example, the low-K material systems, such as $CaO–B_2O_3–SiO_2$ glass-ceramics ($\varepsilon_r=5.9$, $\tan\delta=0.002$ at 0.5 GHz) [6] or $K_2O–CaO–SrO–BaO–B_2O_3–SiO_2$ glass-ceramics ($\varepsilon_r=9.1$, $\tan\delta=1\times10^{-3}$ at 10 MHz) [7] could be sintered below 1000 °C. However, they do not meet the requirement of nearly zero τ_f. Then, we also have reported a new diopside glass–ceramic system showing the promising dielectric properties ($\varepsilon_r=9.1$, $Q\times f=7321$ GHz at 7 GHz, $\tau_f=-71$ ppm/°C) [8], but there is a problem of high τ_f. In this study, we design a reactive route to form the optimum second phase in the diopside material. This second phase forming in matrix not only decreases the τ_f value almost to zero but also increases the quality factors.

2. Experimental procedures

Diopside glass frits were prepared as described in our previous report [8]. Then, the crystallite glass frits added with different amounts (from 0 to 14 wt%) of $MgTiO_3$ ceramic powders were pressed under a loading of 1000 kgf to obtain thin circular pellets (φ15 mm). Specimens were sintered at 950 °C for 4 h. Phase identification of the sintered pellets was carried out using an X-ray diffractometer (M18XHF, MAC Science, Japan) with CuKα radiation. The microstructural features and elemental distribution were studied using an electron probe micro-analysis (EPMA) with backscattered electron imaging (BEI) and wavelength-dispersive spectroscopy (WDS) (JEOL, JXA-8200, Japan). The microwave dielectric properties of sintered samples were determined using a network analyzer HP8722A (Agilent, USA) according to the Hakki and Coleman resonator method [9,10]. The temperature coefficient of resonant frequency of the samples was measured in the temperature range from −30 °C to 80 °C.

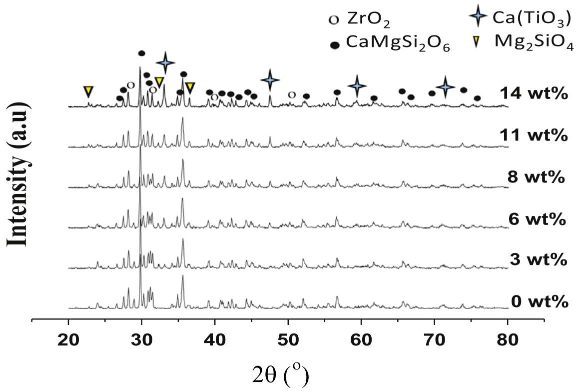

Fig. 1. X-ray diffraction patterns of diopside glass-ceramics added with different amounts of $MgTiO_3$.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of diopside glass-ceramics added with different amounts of $MgTiO_3$ and sintered at 950 °C. The pure $MgTiO_3$ ceramics sintered at 1300 °C also show optimum dielectric properties ($\varepsilon_r=17$, $Q\times f=160{,}000$ GHz, $\tau_f=-50$ ppm/°C) [11]. Fig. 1 shows the formation of additional phases formation, such as $CaTiO_3$ and Mg_2SiO_4. The amount of these secondary phases increases as the $MgTiO_3$ content grows. Fig. 2 shows the densities and dielectric properties of the diopside glass-ceramics with $MgTiO_3$ addition. It was found out that diopside glass-ceramics added with 0–8 wt% of $MgTiO_3$ exhibit high densities owing to wettability and liquid phase sintering of glass with $MgTiO_3$ ceramics. However when added with 11–15 wt% of $MgTiO_3$, the density of resulting glass ceramics decreases, showing such amount of $MgTiO_3$ ceramics addition to be an excess. Both the

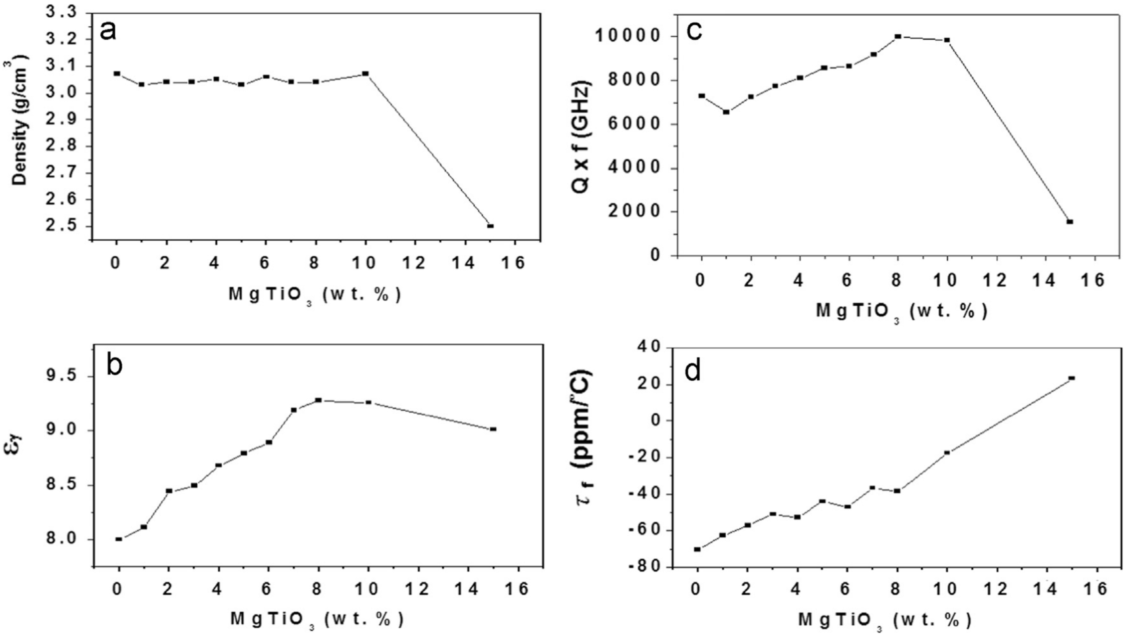

Fig. 2. (a) Density, (b) dielectric constant (c) quality factor and (d) temperature coefficient of resonant frequency of annealed glass frits sintered at 950 °C for 2 h versus the $MgTiO_3$ content.