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Effects of TiO_2 on sinterability and dielectric properties of high-Q forsterite ceramics

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Abstract

High-Q plain forsterite ceramics with $Q{\cdot}f = 240{,}000$ GHz were developed by the usual solid sintering process using raw materials of highly purified MgO and SiO_2. The τ_f (temperature coefficient of the resonant frequency) was negative in range −60 to −70ppm/°C. To adjust this to zero we added rutile with high τ_f (450ppm/°C). The addition of TiO_2 increased dielectric constant (ε_r), did not affect the Q value, but decreased the sintering temperature by about 100 °C for addition of 0.5 to 10 wt.% TiO_2. These results were attributed to increasing the sinterability at low temperature by the TiO_2 and the almost pore-free and glassy-phase free grain boundary microstructures. It was not possible to develop a compostion which had $\tau_f = 0$ ppm/°C, as a result of the chemical reaction between MgO–TiO_2 and TiO_2 during sintering.

Keywords: Dielectric properties; Forsterite; Insulators; Mg_2SiO_4; Microwave dielectric substrates; Silicate; Substrates

1. Introduction

Low permittivity and high-Q dielectric ceramics have recently become of great importance, since ceramic substrates should have a low permittivity (to minimize cross-coupling with conductors and to shorten the time for the electronic signal transition) for the application of advanced substrate materials needed for microwave integrated circuits (MIC). These substrate materials also ought to exhibit high Q dielectric factors in order to maintain overall high-Q circuits by lowering power dissipation. Typical dielectric values for some commonly used for low-permittivity ceramic substates show less reliable properties for the MIC application.[1] The materials show large tanδ in the range of 10^{-3} to 10^{-4} with ε_r of 4–10 measured at 1 MHz. These poor properties were probably attributed to glassy-phase content caused by impurities and various kinds of additives included in the starting material. We have recently succeeded in the synthesis of high purity forsterite ($2MgO{\cdot}SiO_2$) ceramics with high $Q{\cdot}f$, i.e. of the order of 200,000 GHz. This forsterite ceramic demonstrated $Q = 10{,}500$ and ε_r of 6.8 at 23 GHz.[2]

In the present study, forsterite was mixed with TiO_2 in order to control the temperature coefficient (τ_f) of the resonant frequency. TiO_2 addition has often been utilized and succeeded in the control of sintering process and dielectric properties.[3,4] The effects of TiO_2 addition on the sintering behaviour and microwave dielectric properties of forsterite ($2MgO{\cdot}SiO_2$) ceramics are reported.

2. Experimental

High-purity (99.9%) MgO, SiO_2 and TiO_2 powders were used as raw materials. The powder mixture (100 g) for forsterite ($2MgO{\cdot}SiO_2$) compostition was ground for 20 h in a polyethylene bottle with 300 ml distilled water and 100 pieces of polyurethane-coated iron balls 15 mm in diameter. The mixture was dried and calcined in a high-purity alumina crucible at 1200 °C for 3 h in air. After calcination, TiO_2 (rutile or anatase type) was added to the calcined mixture and a second attrition was carried out to reach a homogeneous granulometric distribution within the sample. The powder mixture, with added PVA organic binder (1 wt.%), was pelletized into cylindrical compacts 20 mm in diameter and 8–12

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mm in thickness using a uniaxial press (30 MPa) and cold isostatic press (CIP, 300 MPa). The compacts were sintered at temperatures from 1200 to 1600 °C for 2 h in air.

The apparent density of the sintered sample was measured by the Archimedes' method. The crystalline phase was identified by powder X-ray diffraction (XRD) using CuK_α radiation with Ni filter. The microstructure observation and quantitative analysis were performed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) respectively. The dielectric constants and unloaded Q values were measured in the TE_{011} mode using the Hakki and Coleman method.[5] The temperature coefficient of resonant frequency (τ_f) and temperature coefficient of permittivity (τ_ε) values were evaluated in the temperature range between 20 and 80 °C.

3. Results and discussion

The sintering temperatures were determined on the basis of the apparent densities of sintered forsterite ceramics without TiO_2 and with 1 wt.% TiO_2 (rutile and anatase). Densities are shown as a function of sintering temperature in Fig. 1(a); the sintering temperature of the ceramics prepared with 1 wt.% TiO_2 (both rutile and anatase) decreased by about 100 °C compared with samples prepared with no additive. Maximum density yielded the maximum dielectric constant (ε_r) and the minimum dielectric loss (tanδ) as shown in Fig. 1(a) and (b). We selected the rutile phase TiO_2 for additions, because rutile was more effective than anatase for improving the properties as evidenced in Fig. 1(a)–(c). Fig. 2 shows the relationships between the apparent densities and sintering temperatures for $2MgO{\cdot}SiO_2$

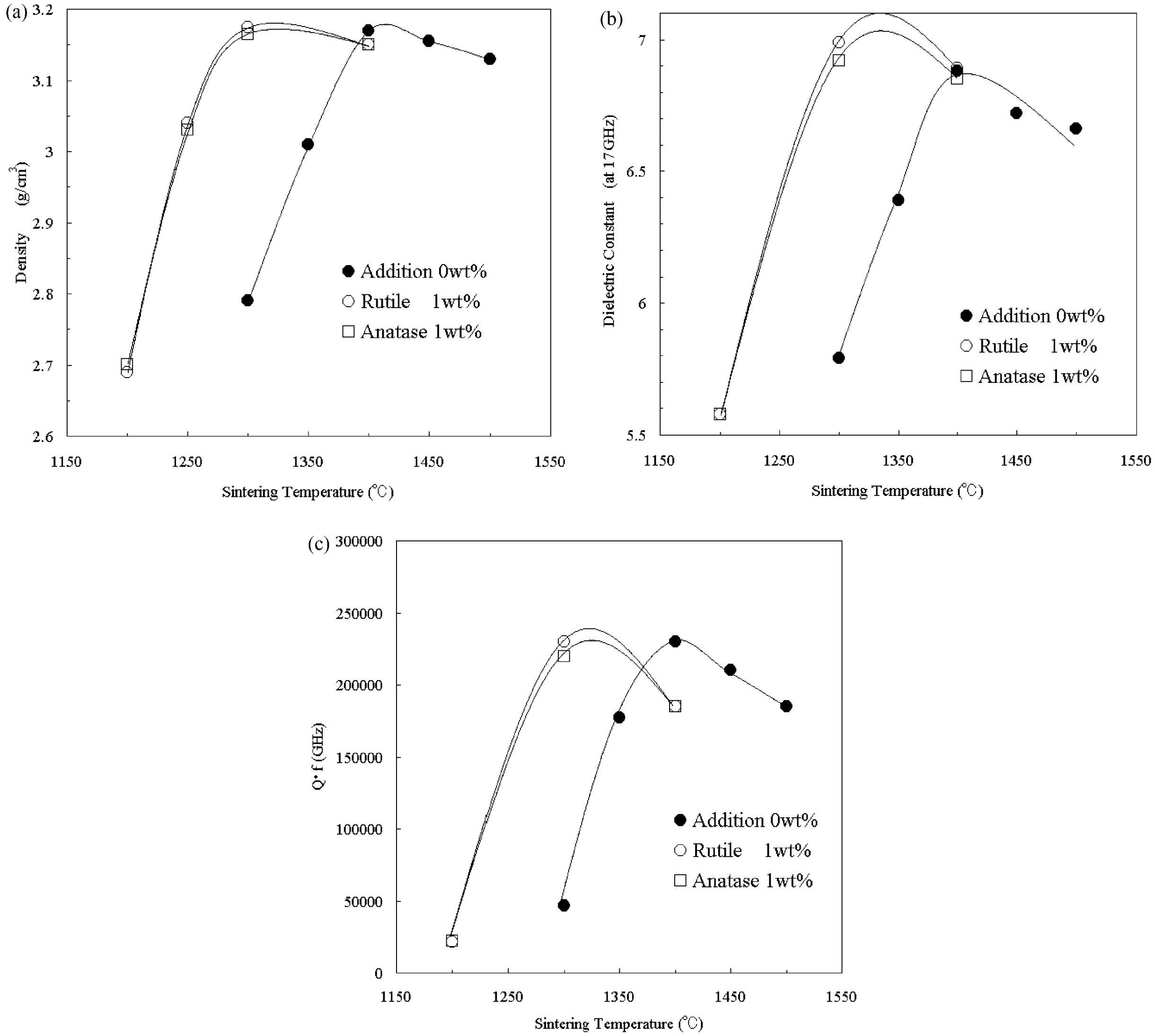


Fig. 1. The relationship between (a) density, (b) dielectric constant and (c) $Q{\cdot}f$ and sintering temperature of $2MgO{\cdot}SiO_2$ modified with TiO_2 addition.

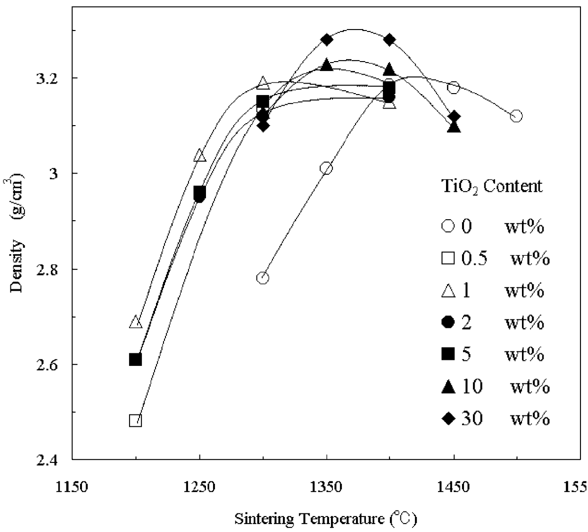


Fig. 2. The relationship between density and sintering temperature of $2MgO{\cdot}SiO_2$ modified with TiO_2 as a function of TiO_2 content.

modified with TiO_2 from 0.5 to 30 wt.%. It was observed that addition of TiO_2 from 0.5 to 5 wt.% decreased the sintering temperature by 100 °C compared with that for samples prepared with no additive. However, samples prepared with addition of TiO_2 over 10 wt.% did not sinter at 1300 °C, because the sintering temperature was increased by about 50 °C.

The dielectric properties of forsterite modified with TiO_2 from 0.5 to 30 wt.% are shown in Fig. 3. The temperature coefficient of resonant frequencey (τ_f) and temperature coefficient of dielectric coefficient (τ_ε) show little dependence on the amount of TiO_2 in the samples Fig. 3c. We expected that τ_f would improve to near 0 ppm/°C according to addition of TiO_2 based on a mixing rule for composite materials (in this case forsterite and TiO_2). From the rule of mixing, we calculated the compostion at which the τ_f becomes 0 ppm/°C to be 13.3 wt% of TiO_2. However we could not obtain a composition which exhibited $\tau_f = 0$, but obtained samples

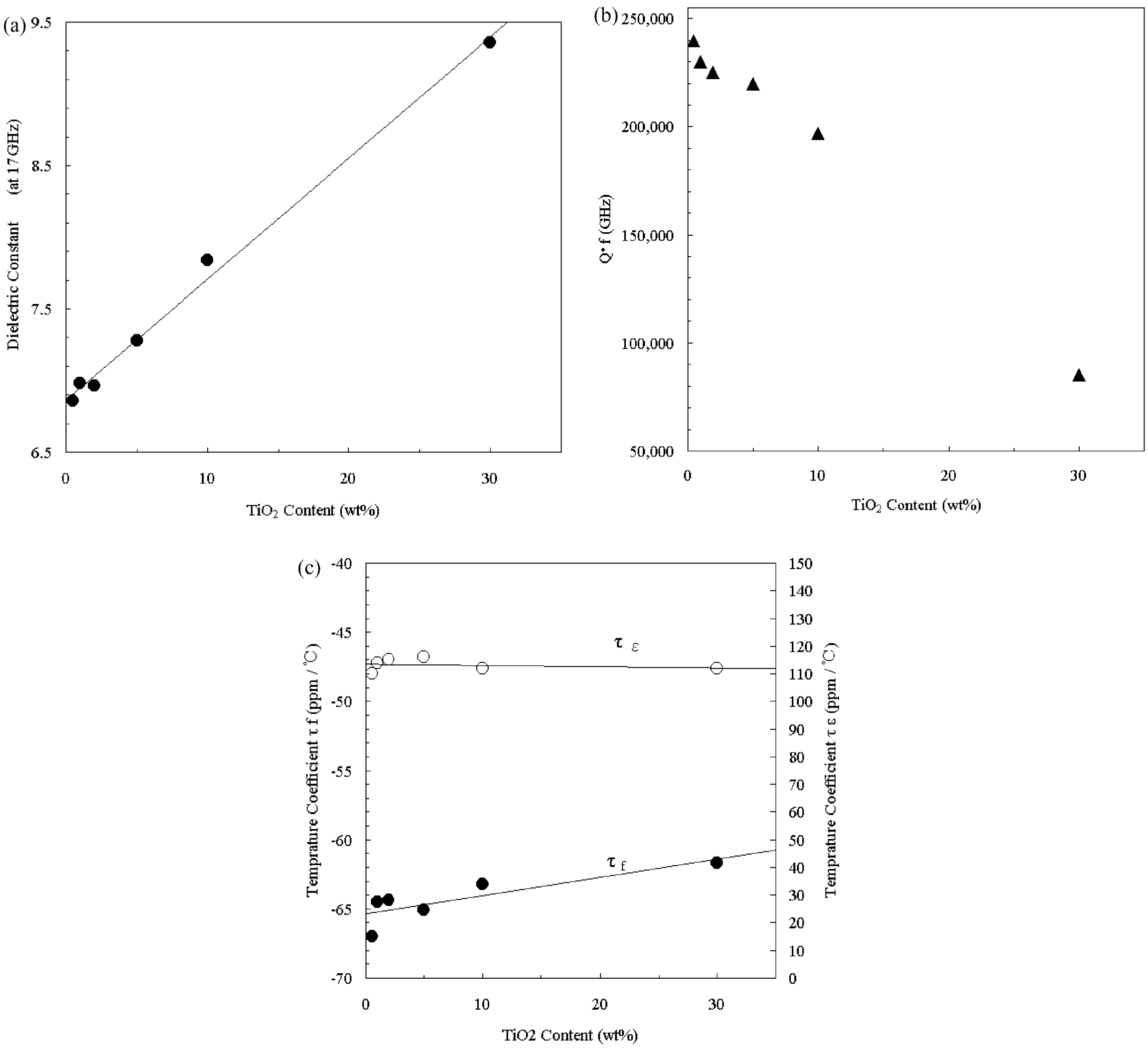
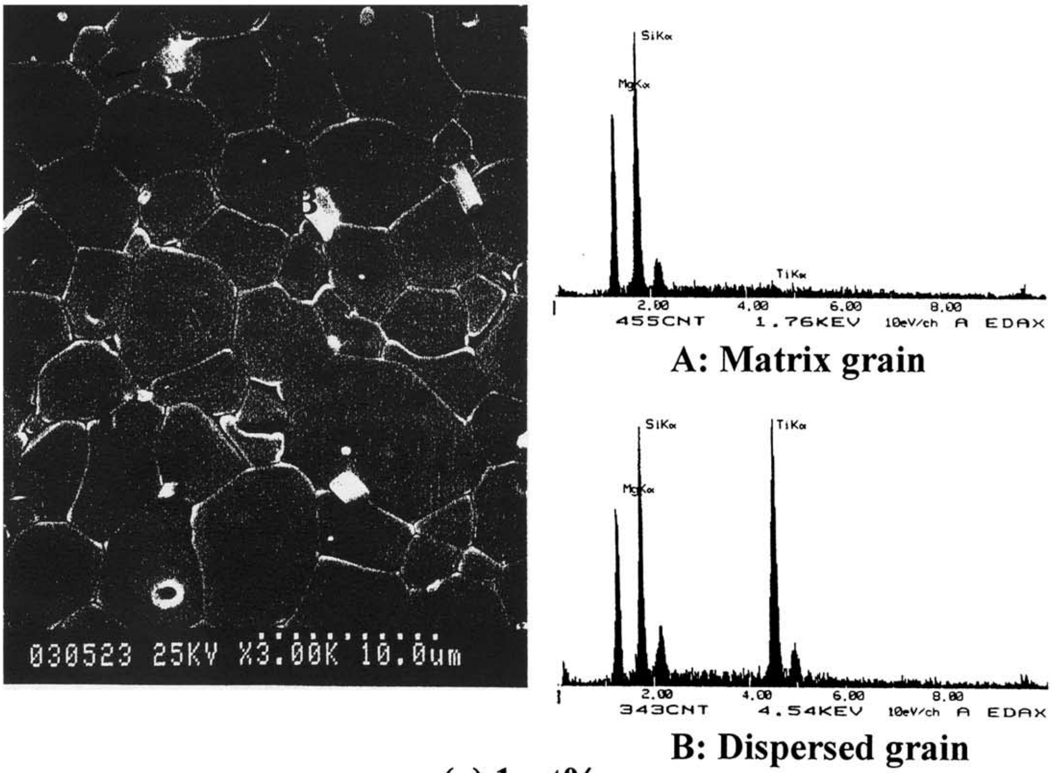
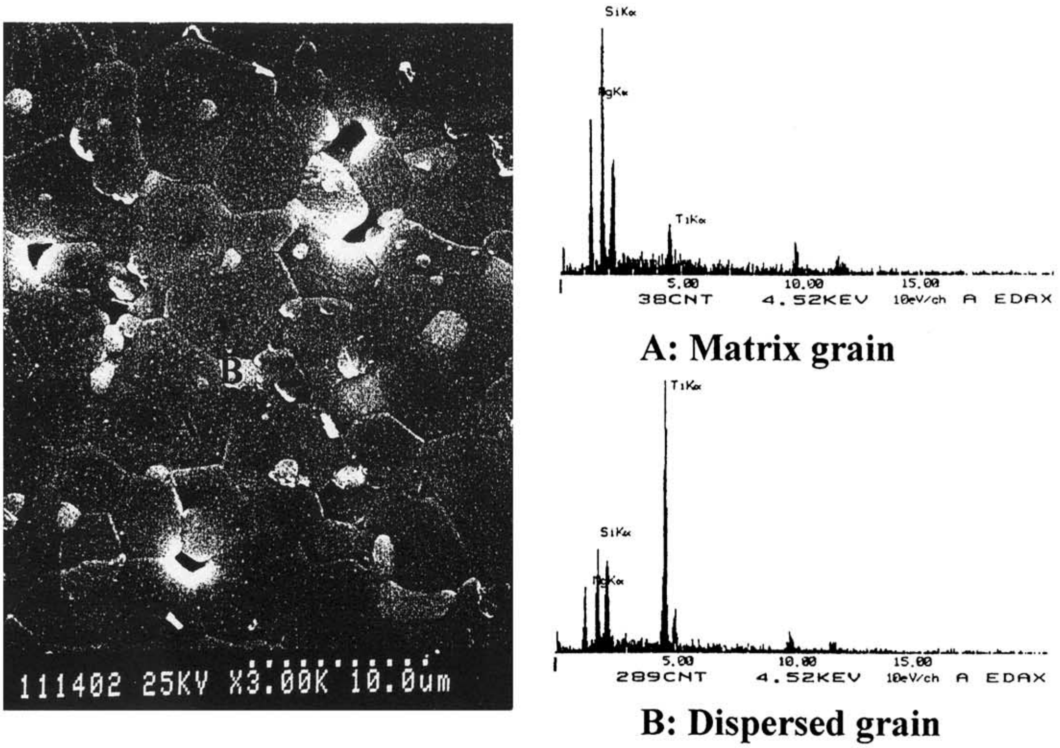


Fig. 3. The relationship between (a) dielectric cosntant, (b) $Q{\cdot}f$ and (c) the τ_f and τ_ε and TiO_2 content of $2MgO{\cdot}SiO_2$.

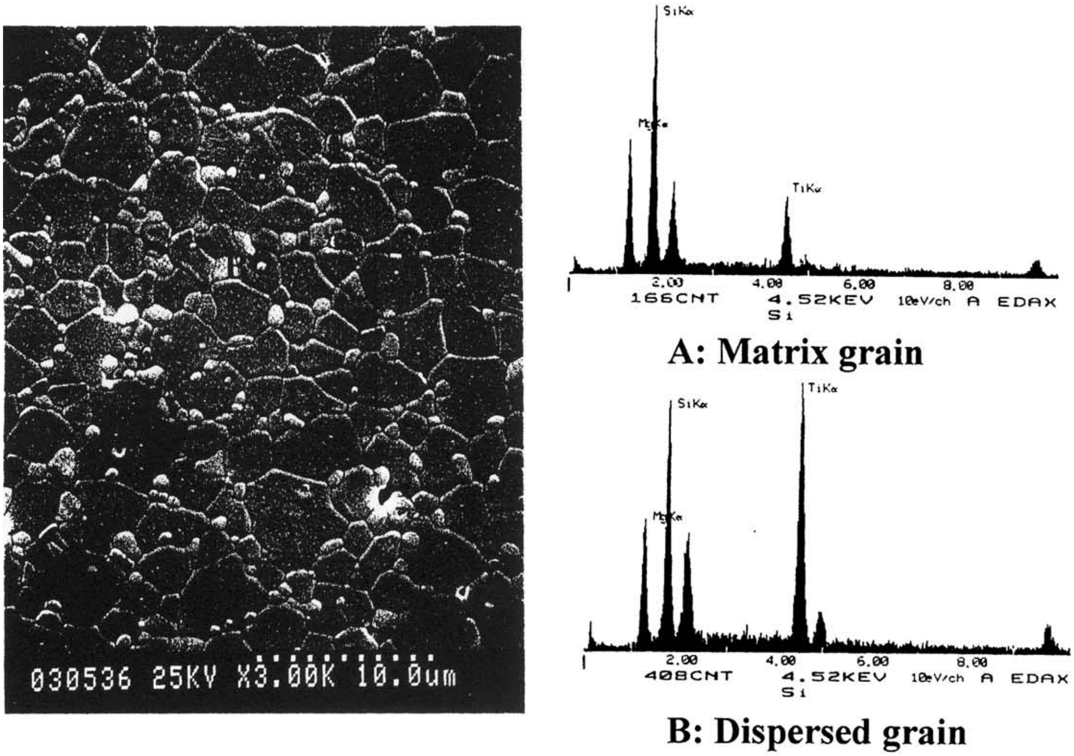


(a) 1 wt%

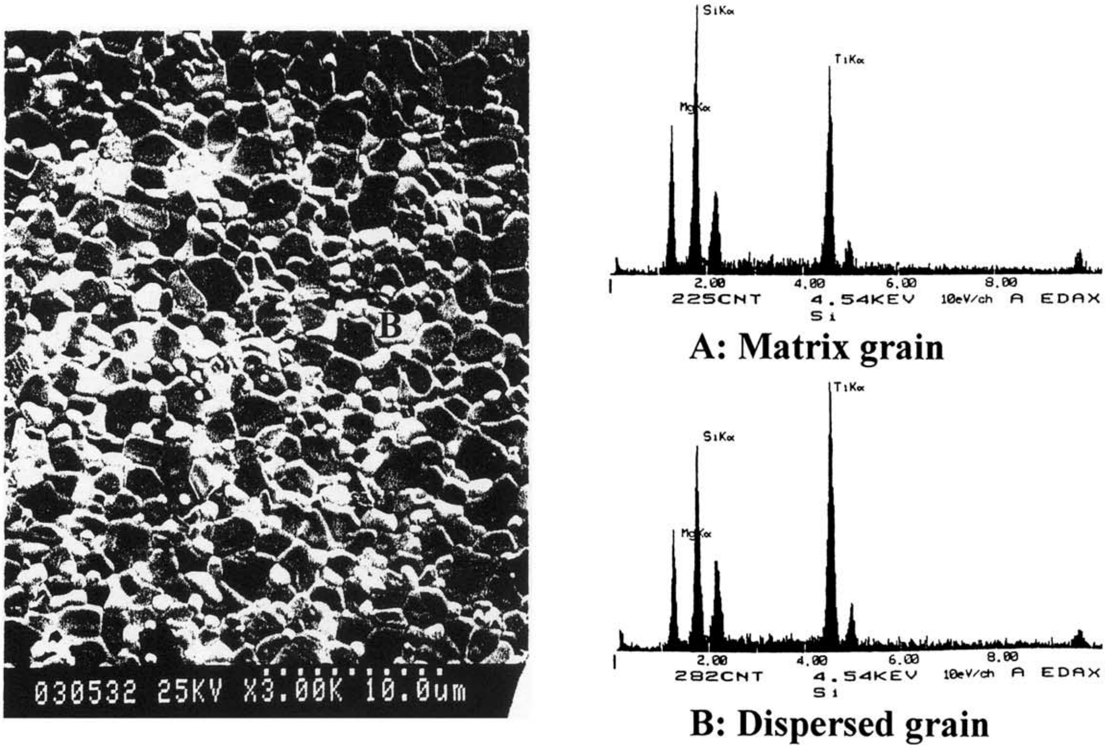


(b) 5 wt%

Fig. 4. SEM micrograph and EDX spectra of $2MgO{\cdot}SiO_2$ ceramics with TiO_2 of (a) 1 wt.%, (b) 5 wt.%, (c) 10 wt.% and (d) 30 wt.%.



(c) 10 wt%



(d) 30 wt%

Fig. 4 (*continued*).

with almost unchanging τ_f at −63 ppm/°C. A similar behaviour was observed for the temperature coefficient of permittivity τ_ε. The experimentally obtained value was much lower than the expected one from the mixing rule. These results suggest that the TiO_2 additive, especially at 10–30 wt.%, resulted in large differences in the τ_f and τ_ε from the calculated values. This may be due to the fact that the TiO_2 additive reacted with the MgO–SiO_2 and did not remain as a separate component in the composite. The powder XRD analysis of sintered forsterite ceramics modified with TiO_2 up to 30 wt.% revealed that the rutile phase disappeared in all sample compositions, due to the reaction with MgO–SiO_2. For upto 10 wt.% TiO_2 addition, only forsterite exists. The phase $MgTi_2O_5$ appeared and increased as the amount of TiO_2 increased from 10 to 30 wt.%. According to the MgO–SiO_2–TiO_2 ternary phase diagram,[6] TiO_2 does not exist as a single phase until over 50 wt.%. If composites with forsterite and TiO_2 are desired for τ_f with 0 ppm/°C resonator, the sintering procedure needs to be considered in detail.

According to the amount of TiO_2 in our system, ε_r increased linearly as shown in Fig. 3(a). It seems that this increase of ε_r is caused by the increase in density (see Fig. 2). On the other hand, the Q value decreased gradually by addition of TiO_2 up to 10 wt.%, but there was an enormous decrease in Q value for TiO_2 additions of 10–30 wt.% as shown in Fig. 3(b).

Fig. 4 shows SEM micrographs and EDX spectra of $2MgO{\cdot}SiO_2$ ceramics with TiO_2 of (a) 1wt.% and (b) 5wt.% sintered at 1300 °C, (c) 10 wt.% and (d) 30 wt.% sintered at 1350 °C for 2 h. These ceramics had microstructures which were almost pore free and glassy-phase free at the grain boundaries. This seemed to be due to the increasing sinterability of TiO_2 and forsterite prepared from high-purity raw materials. The size of grains of these ceramics showed a tendency to increase linearly with increasing TiO_2 from 0.5 to 5 wt.%. In contrast, the grain size decrease linearly with increasing amount TiO_2 additive from 5 to 30 wt.%. With an increase of TiO_2, a white secondary phase, which consists of MgO–SiO_2–TiO_2 [EDX analysis; see Fig. 4(a)–(c)] increased linearly with increasing TiO_2 from 1 to 10 wt.%, while it increased significantly at 30 wt.%. The peak corresponding to the Ti K_α could not be detected from matrix grains of samples sintered with 1 wt.% TiO_2 as shown in Fig. 4(a). However, it increased gradually in samples prepared with 5–30 wt.% as shown in Fig. 4(b)–(d).

4. Conclusions

The dielectric properties and sinterability of forsterite ceramics modified with TiO_2 exhibited excellent high Q values ($Q{\cdot}f = 240{,}000$ GHz). Addition of 0.5–5 wt.% TiO_2 increased dielectric constants (ε_r), did not significantly affect the Q value (Q value 10,000 at 16 GHz), but decreased the sintering temperature by about 100 °C. These changes seemed to be caused by the increasing sinterability due to additions of TiO_2; almost pore free and glassy-phase free microstructures were developed. The compostion prepared with addition of 1 wt.% of TiO_2 exhibited a high $Q{\cdot}f$ value = 230,000 GHz with $\varepsilon_r = 7.0$ and $\tau_f = -65$ppm/°C. Both the τ_f and τ_ε were almost independent of increasing TiO_2 content. This behaviour is attributed to the chemical reaction between MgO–SiO_2 and TiO_2 during sintering.

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