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Paper

Zero Temperature Coefficient τ_f and Sinterability of Forsterite Ceramics by Rutile Addition

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The temperature coefficient (τ_f) of the resonant frequency for pure forsterite (Mg_2SiO_4) ceramics was negative in the range from −60 to −70 ppm/°C. To adjust the τ_f value to zero, rutile (TiO_2) with the high τ_f (450 ppm/°C) was added. When sintering temperature was selected as low as possible, TiO_2 remained in the forsterite specimen, which raised τ_f from a negative to positive values. For instance, the 30 wt% TiO_2 added forsterite ceramics sintered at 1200°C yield a high density (3.3 g/cm^3), which same as that of the same forsterite ceramics sintered at 1350°C. A part of added TiO_2 works for sintering aid and residual ones do for lowering the τ_f value. Forsterite ceramics have $\tau_f = 0$ ppm/°C, $\varepsilon_r = 11$ and $Q \cdot f = 82000$ GHz, when they contains 24 wt% of TiO_2 and sintered at 1200/°C for 2 h.
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Key-words : *Forsterite, Microwave dielectric materials, Quality factor, Temperature coefficient of resonant frequency (τ_f)*

1. Introduction

Recently, microwave telecommunication has been developed for a wide range of applications, such as mobile phone, wireless LAN and Intelligent Transport System (ITS). Utilized microwave frequency has also increased from microwave to millimeter range because transmittance of large quantity of information with high speed. Millimeter-wave dielectric ceramics for these telecommunicating devices are necessary to have a high quality factor ($Q \cdot f$), a low dielectric constant (ε_r) and a nearly zero temperature coefficient of resonant frequency (τ_f). Andou *et al.*[1] succeeded in the preparation of the forsterite ceramics with the high $Q \cdot f$ and the low ε_r using highly purified MgO and SiO_2 as raw materials, but the ceramics showed a large negative τ_f of −67 ppm/°C. To adjust the negative τ_f value to zero we selected rutile (TiO_2) with large amount of τ_f (450 ppm/°C), but this has not been succeeded.[2] The main reason was thought to be due to the disappearance of rutile phase in the microstructure because the sintering temperature was so high that TiO_2 reacted with forsterite phase.[3] In this study, improvement of the τ_f for the forsterite ceramics was attempted by adding TiO_2, which remain as a residual phase even after sintering treatment.

2. Experimental procedure

High-purity (99.9%) MgO and SiO_2 powders were used as raw materials. These powders were mixed for 20 h in a polyethylene bottle with 300 ml distilled water and using 100 pieces of polyurethane-coated iron balls with 15 mm in diameter. The mixture was dried and calcined in a high-purity alumina crucible at 1150/°C for 3 h in air. Then, high-purity (99.5%) TiO_2 (rutile type) was added in a range from 10 to 40 wt% to the calcined mixture. After addition of the PVA organic binder (1 wt%), a second attrition was carried out to reach a homogeneous distribution with average particle size of about 1 μm. The powder was pelletized into cylindrical compacts of 12 mm in diameter and 5-7 mm in thickness using a uniaxial press (86 MPa) and a cold isostatic press (200 MPa). The compacts were divided into three groups and sintered as follows. The first group was the Mg_2SiO_4 ceramics added with 30 wt% of TiO_2 and sintered at 1200, 1250, 1300, 1350 and 1400°C for 2 h. The second group was the Mg_2SiO_4 ceramics added with 10, 20 and 30 wt% of TiO_2 and sintered at 1400°C for 2 h. The third group was the Mg_2SiO_4 ceramics added with 20, 25, 30 and 40 wt% of TiO_2 and sintered at 1150 to 1200°C for 2 h. The crystalline phases of sintered pellets were investigated by a X-ray powder diffraction (XRPD). After the surface of specimens was ground and polished, the apparent density were measured by the Archimedes' method. The microstructure was observed by a scanning electron microscope (SEM). The microwave dielectric properties (ε_r, $Q \cdot f$ and τ_f) were evaluated using a pair of parallel conducting Ag plates in the TE_{011} mode by a modified Hakki and Coleman's method.[4),5)]

3. Results and discussion

Figure 1 shows the relationship between (a) apparent density, (b) $Q \cdot f$, (c) ε_r and (d) τ_f of the Mg_2SiO_4 ceramics added with 30 wt% of TiO_2 as a function of the sintering temperature from 1200 to 1400°C. The apparent densities keep high values of ca. 3.3 g/cm^3 in the samples sintered at temperatures from 1200°C to 1350°C. This result indicates that these ceramics make it possible to be sintered even at 1200°C. Namely, TiO_2 acts as a sintering aid for increasing sinterability of forsterite. The addition of 30 wt% of TiO_2 reduced the sintering temperature from 1400°C for the pure forsterite ceramics to 1200°C.[1)] However, the apparent density decreased abruptly in the sample sintered at 1400°C because of a chemical reaction of TiO_2 with forsterite. The dielectric constant of the sample sintered at 1200°C showed a maximum value, and the $Q \cdot f$ value had maximum for the sample sintered at 1250°C. On the other hand, the τ_f changed abruptly from a negative value to positive one and for example, the τ_f is 12.7 ppm/°C for the sample sintered at 1200°C.

Figure 2 shows the XRPD patterns of the Mg_2SiO_4 ceramics added with 30 wt% of TiO_2 sintered at 1200 to 1400°C for 2 h. For the sample sintered at 1200°C, the peaks of $MgTi_2O_5$ and $MgSiO_3$ are observed and the peaks of unreacted TiO_2 also appear. It is considered that the large positive τ_f of TiO_2 (450 ppm/°C) could compensate the negative τ_f (−67 ppm/°C) of Mg_2SiO_4. The τ_f of the Mg_2SiO_4 ceramics added with 30 wt% of TiO_2 and sintered at 1200°C was 12.7 ppm/°C as indicated in Fig. 1(d). However, the τ_f of the other specimens sintered at temperatures from 1250 to 1400°C showed a constant value of about −60 ppm/°C. The addition of rutile played two

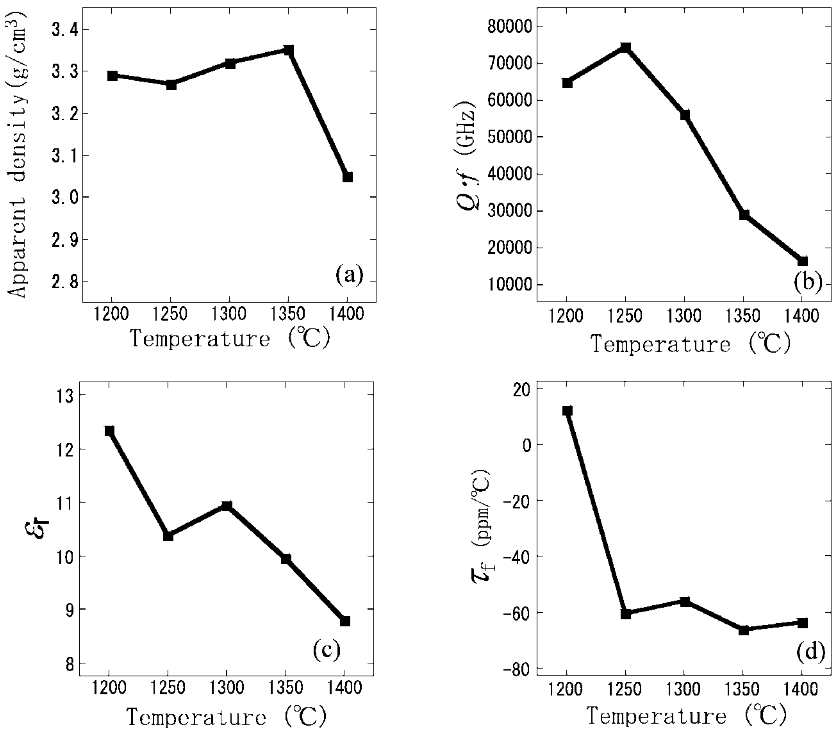

Fig. 1. The relationship between (a) relative density, (b) $Q{\cdot}f$, (c) ε_r and (d) τ_f of the Mg_2SiO_4 ceramics added 30 wt% of TiO_2 as a function of the sintering temperature from 1200 to 1400°C.

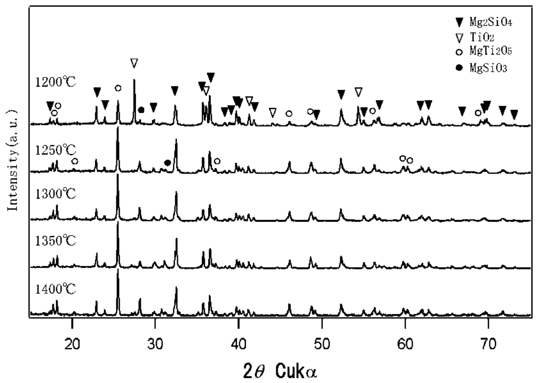

Fig. 2. The of XRPD patterns of the Mg_2SiO_4 ceramics added 30 wt% of TiO_2 sintered at 1200 to 1400°C for 2 h.

roles; one is a sintering aid for forsterite, and the other is improvement of τ_f as an unreacted rutile phase. In the specimens sintered at 1200°C, these two roles are clearly observed. Some of added rutile reacted with Mg_2SiO_4 to form $MgTi_2O_5$ phase as the following chemical reaction.

$$Mg_2SiO_4 + 2TiO_2 \longrightarrow MgTi_2O_5 + MgSiO_3$$

On the other hand, the residual rutile works for improving τ_f. Since the diffraction peaks of the rutile decreased with increasing the sintering temperature, the second role is considered to work weaker. The important finding in this study is an unreacted TiO_2 phase improved negative τ_f of forsterite ceramics.

Figure 3(a) shows XRPD patterns of the Mg_2SiO_4 ceramics added 20 to 40 wt% of TiO_2 and sintered at 1200°C for 2 h. The strong intensity of the diffraction peaks of TiO_2 did not depend on the amounts of TiO_2. In contrast, the intensity of

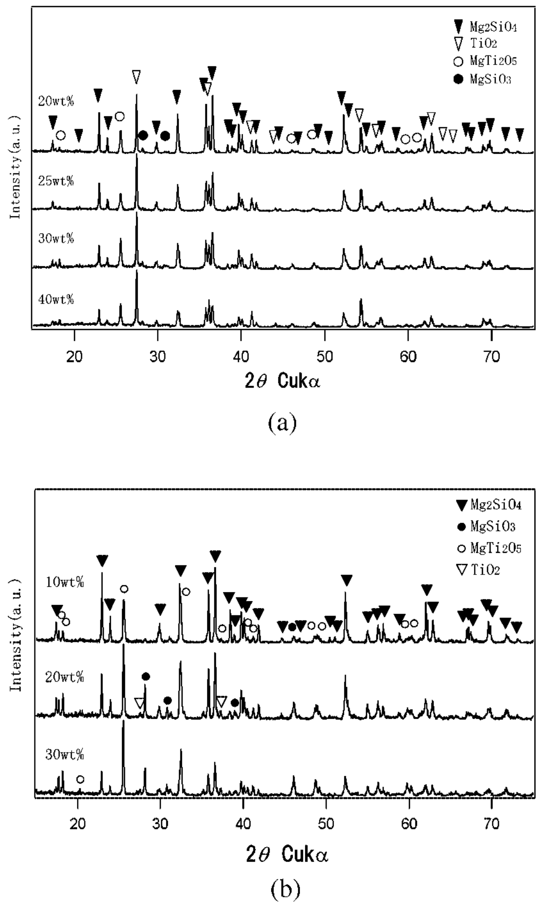

Fig. 3. XRPD patterns of the Mg_2SiO_4 ceramics added (a) 20 to 40 wt% of TiO_2 and sintered at 1200°C for 2 h, (b) 10 to 30 wt% of TiO_2 and sintered at 1400°C for 2 h.

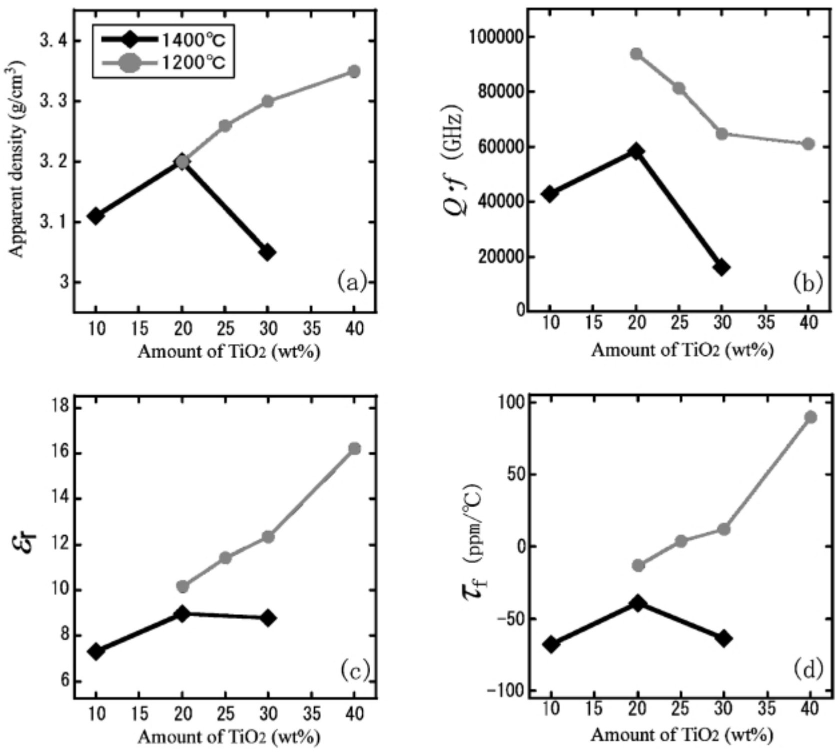

Fig. 4. The relationship between (a) apparent density, (b) $Q\cdot f$, (c) ε_r and (d) τ_f of the Mg_2SiO_4 ceramics added 10 to 40 wt% of TiO_2 and sintered at 1200°C and 1400°C for 2 h as a function of TiO_2 content.

$MgTi_2O_5$ increased gradually, particularly in the sample with addition of 20 and 30 wt% addition of TiO_2. This was thought to be a result of chemical reaction among MgO, SiO_2 and TiO_2. On the other hand, XRPD patterns of Mg_2SiO_4 decreased gradually with increasing TiO_2 content from 25 to 40 wt%. The both peaks of unreacted TiO_2 and $MgTi_2O_5$ appeared in the XRPD patterns. Fig. 3(b) shows XRPD patterns of the Mg_2SiO_4 ceramics added 10 to 30 wt% of TiO_2 and sintered at 1400°C for 2 h. Diffraction peaks of TiO_2 appear slightly in the sample with 20 to 30 wt% addition of TiO_2. The diffraction peaks of $MgSiO_3$ and $MgTi_2O_5$ appeared in all the samples. The intensity of $MgTi_2O_5$ increased with increasing TiO_2 content, but intensity of Mg_2SiO_4 decreased almost linearly. TiO_2 diffraction peak hardly appears but slightly appears only in the samples with 20 to 30 wt% addition of TiO_2. **Figure 4** shows the relationship between (a) apparent density, (b) $Q\cdot f$, (c) ε_r and (d) τ_f of the Mg_2SiO_4 ceramics added 10 to 40 wt% of TiO_2 and sintered at 1200°C and 1400°C for 2 h as a function of TiO_2 content. We could not measure the microwave dielectric properties of the specimens sintered at 1150°C for 2 h, because frequency responses did not appear due to low $Q\cdot f$. In the case of the samples sintered at 1200°C, the τ_f of Mg_2SiO_4 ceramics added with TiO_2 increased linearly with increasing TiO_2 addition, the τ_f changed from negative to positive values between 20 and 25 wt% addition of TiO_2. The τ_f showed 3.95 ppm/°C in the case of 25 wt% TiO_2 content. It is inferred that $\tau_f = 0$ ppm/°C, $\varepsilon_r = 11$ and $Q\cdot f = 82000$ GHz in the Mg_2SiO_4 ceramics is attainable for 24 wt% TiO_2 ceramic composite sintered at 1200°C for 2 h. The apparent density and the dielectric constant increased linearly with increasing TiO_2 addition. It was observed clearly an increase of apparent density and it was attributed to addition of TiO_2 with higher density (4.24 g/cm^3) than Mg_2SiO_4 ceramics (3.22 g/cm^3). The $Q\cdot f$ decreased abruptly in the case from 20 to 30 wt% addition of TiO_2, and gradually decreased for the samples with TiO_2 addition from 30 to 40 wt%. However, the sample exhibits higher $Q\cdot f$ than 60000 GHz. A large deterioration in the $Q\cdot f$ value occurred at 1400°C. This was thought to be due to the formation of $MgTi_2O_5$ and $MgSiO_3$. While the τ_f improved in the sample sintered at 1200°C, the τ_f showed large negative values in all TiO_2 added specimens sintered at 1400°C. This result indicates that the 1400°C is too high for remaining of TiO_2 phase. Therefore, properties including density, $Q\cdot f$, ε_r and τ_f were worse than those obtained in the sample sintered at 1200°C. **Figure 5** shows SEM micrograph of the Mg_2SiO_4 with 25 wt% TiO_2 ceramic composite sintered at 1200°C for 2 h. The microstructure was composed by grains of forsterite (light

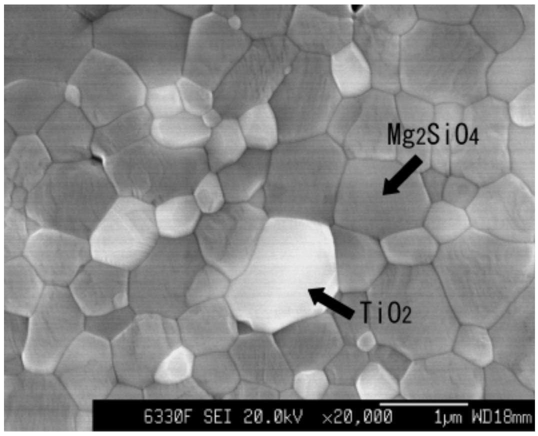

Fig. 5. A SEM micrograph of the Mg_2SiO_4 with 25 wt% TiO_2 ceramic composite sintered at 1200°C for 2 h.

gray grains) and ones of rutile (white grains) and densified to the level of free of pore and glassy-phase at grain boundaries. This seemed to be due to the enhanced sinterability by excess TiO_2 addition.

4. Conclusion

To adjust the τ_f of forsterite ceramics to 0 ppm/°C which has negative τ_f of −65 ppm/°C, rutile with the high τ_f was added to forsterite ceramics. We found that the high density forsterite ceramics could sinter at 1200°C when 30 wt% TiO_2 was added in forsterite ceramics. Moreover, we got the forsterite ceramics with the $\tau_f = 0$ ppm/°C at 24 wt% TiO_2 added ceramics, when the forsterite ceramics have sintered as a function of TiO_2 composition added at 1200°C. The ε_r and the $Q \cdot f$ of the 24 wt% rutile added forsterite ceramics are 11 and 82000 GHz, respectively.

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References

1) Andou, M., Tsunooka, T., Higashida, Y., Sugiura, H. and Ohsato, H., Abstract for Microwave Materials and Their Applications, pp. 141, 1–3 Sept. 2002 York, UK.
2) Tsunooka, T., Andou, M., Higashida, Y., Sugiura, H. and Ohsato, H., *J. Eur. Ceram. Soc.*, Vol. 23(14), pp. 2573–2578 (2003).
3) Ohsato, H., Tsunooka, T., Andou, M., Ohishi, Y., Miyauchi, Y. and Kakimoto, K., *J. Korean Ceram. Soc.*, Vol. 40, pp. 350–353 (2003).
4) Hakki, B. W. and Coleman, P. D., *IRE Trans.Microwave Theory & Tech.*, MTT-8, pp. 402–410 (1960).
5) Kobayasi, Y. and Kato, M., *IEEE Trans. Microwave Theory & Tech.*, MTT-33, pp. 586–592 (1985).