

Mg₂SiO₄–TiO₂ composite ceramics prepared using a liquid phase deposition process

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Abstract Forsterite (Mg₂SiO₄) indicates a high quality factor (Qf) of 270,000 GHz and a low dielectric constant ϵ_r of 6.8, which are applicable for microwave and millimeter-wave dielectric devices. However, a large negative temperature coefficient of resonant frequency (τ_f) of -73 ppm/°C hinders stability. Actually, Mg₂SiO₄–TiO₂ composite ceramics prepared by ordinary solid state reaction showed improved τ_f to 0 ppm/°C. However, Qf of the composite ceramics decreased because other phases such as MgTi₂O₅, MgTiO₃ and MgSiO₃ were created in the reaction between TiO₂ and Mg₂SiO₄ during sintering. This study uses a different process to prepare the Mg₂SiO₄–TiO₂ composite ceramics to prevent the production of the secondary phase. Porous Mg₂SiO₄ ceramics were prepared by sintering Mg₂SiO₄ with pore-forming agents. Then, TiO₂ was inserted into the pores using liquid phase deposition (LPD). Deposited TiO₂ in the pores was anatase form. The increase of the inserted anatase TiO₂ amount contributed to improvement of τ_f .

Keywords Microwave dielectric properties · LPD process · Mg₂SiO₄–TiO₂ composite ceramics · Porosity

1 Introduction

Dense forsterite (Mg₂SiO₄) ceramics possess both a high quality factor (Qf) of 270,000 GHz and a low dielectric

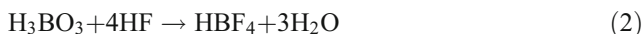
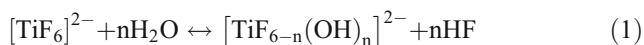
constant ϵ_r of 7.8. The microwave dielectric properties are desirable to develop microwave or millimeter-wave telecommuting applications used for filters, resonators, etc. However, Mg₂SiO₄ ceramics indicate a large negative temperature coefficient of resonant frequency (τ_f) of -73 ppm/°C [1, 2]. For microwave telecommunications, τ_f of 0 ppm/°C is necessary to maintain frequency stability in various climates. To improve τ_f of the Mg₂SiO₄, we previously attempted to produce Mg₂SiO₄–TiO₂ composite ceramics using a conventional solid-state reaction. Rutile TiO₂ shows a large positive value of $\tau_f=450$ ppm/°C. Consequently, the composite ceramics showed τ_f of 3.95 ppm/°C by appending 25 wt% TiO₂ [3, 4]. Unfortunately, the secondary phases of MgSiO₃, MgTi₂O₅ and MgTiO₃ affect the microwave dielectric properties in the resultant composite ceramics. This study undertakes a different process to prepare the Mg₂SiO₄–TiO₂ composite ceramics to prevent production of the secondary phase. Particularly, we emphasize liquid phase deposition (LPD), which is advantageous to prepare ceramic oxides at lower sintering temperatures [5, 6]. Our strategy to prepare Mg₂SiO₄–TiO₂ composite ceramics is as follows. First, we investigate conditions for preparation of porous Mg₂SiO₄ ceramics. Then, we insert TiO₂ into the pores of the porous Mg₂SiO₄ ceramics by applying LPD. In a previous study, we identified the possibility of inserting TiO₂ into porous Mg₂SiO₄ using LPD [7]. The amount of the TiO₂ inserted into the Mg₂SiO₄ porous ceramics was increased several times using LPD. However, the small amount of TiO₂ deposited using one-time LPD remains as a problem. We therefore investigate more effective conditions to deposit TiO₂ into the porous Mg₂SiO₄ ceramics by one-time LPD. Particularly, we investigate effects of concentrations of TiO₂ precursor solutions: H₃BO₃ and (NH₄)₂TiF and difference in two LPD processes.

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2 Experimental

High-purity raw materials of $\text{Mg}(\text{OH})_2$ (99.98%) and SiO_2 (99.9%) were weighed according to their stoichiometric ratios and were then ball-milled for 24 h using zirconia balls as the grinding media and ethanol as the solvent. After drying, the powder was calcined at 1150 °C for 2 h in air. The Mg_2SiO_4 calcined powders were mixed with two pore-forming agents: PMMA and kynol. The PMMA particles are almost spherical, with average particle size of 5.0–1.5 μm . Kynol is fiber-shaped and typically 14 μm and 200 μm length. The mixed powder was pressed into a cylinder with uniaxial pressure of 7.84 MPa. Subsequently to the first step, some was then pressed using cold isostatic pressing (CIP) up to 200 MPa. These pellets were then sintered in air at 1400 °C for 2 h.

We tried to deposit TiO_2 into pores of the porous Mg_2SiO_4 using the following LPD process.



Reaction (1) is shifted from the left side to the right side if the F^- ions are consumed by reactions (2) [6].

Figure 1 shows that we investigated two processes to deposit TiO_2 efficiently in the Mg_2SiO_4 pores using LPD.

Process I The porous Mg_2SiO_4 ceramics were exhausted in a vacuum system and then immersed in ammonium hexafluorotitanate $[(\text{NH}_4)_2\text{TiF}_6]$ with distilled water. Then, boric acid (H_3BO_3) was mixed in the solution. The porous sample was maintained in the mixed solutions at 70 °C for 24 h. Subsequently, the sample was taken from the solution and dried. Finally, the sample was fired at 700 °C for 2 h.

Process II Porous Mg_2SiO_4 ceramics were exhausted in a vacuum system and then immersed in ammonium hexafluorotitanate $[(\text{NH}_4)_2\text{TiF}_6]$ with distilled water. Then the samples were taken from the ammonium hexafluorotitanate solution. After drying, the sample was immersed in a boric acid (H_3BO_3) solution. The porous sample was maintained in the mixed solutions at 70 °C for 24 h. After that, the sample was taken from the solution and dried. Finally, the sample was fired at 700 °C for 2 h.

The concentrations of the solutions were 0.2–0.6 mol/l for $(\text{NH}_4)_2\text{TiF}_6$ and 0.4–1.2 mol/l for H_3BO_3 . The weight percentage of the deposited TiO_2 was estimated from the difference in weight between the Mg_2SiO_4 porous sample and the sample after deposition of TiO_2 and firing at 700 °C.

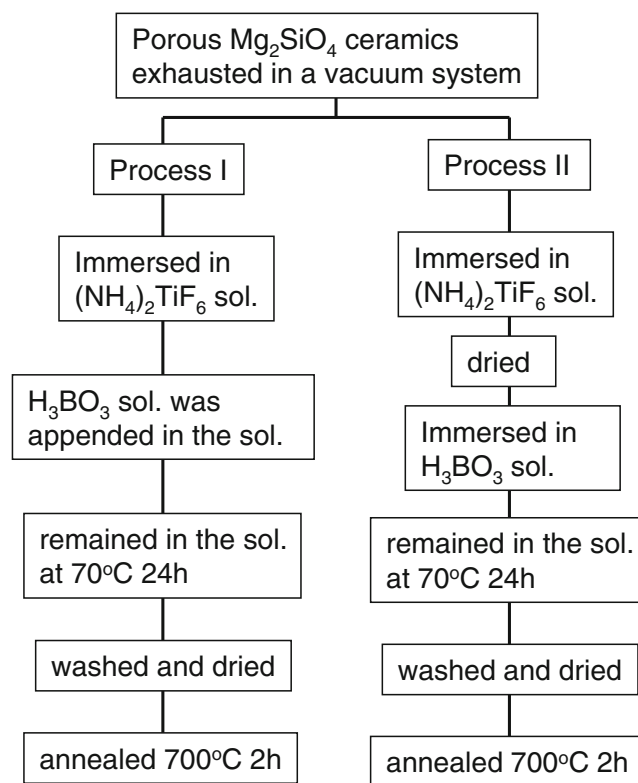


Fig. 1 Scheme showing the LPD deposit processes

Porosities of the Mg_2SiO_4 porous samples and the TiO_2 deposited samples were estimated according to the following relation. The measurement accuracy of the porosities was within $\pm 1\%$.

$$\text{Open porosity} = \frac{W_3 - W_1}{W_3 - W_2} \times 100 \quad (3)$$

$$\text{Closed porosity} = \frac{(W_1 - W_2) - W_1 \rho_w / \rho}{W_3 - W_2} \times 100 \quad (4)$$

$$\text{Total porosity} = \text{open porosity} + \text{closed porosity} \quad (5)$$

In those equations, the following variables are used.

W_1 (g)	mass of the dried sample
W_2 (g)	mass of the sample in distilled water
W_3 (g)	mass of the wet sample
ρ_w (cm^3/g)	density of water
ρ (cm^3/g)	density of Mg_2SiO_4

The respective microstructures of the samples were observed using scanning electron microscopy (SEM). The sample phases were investigated using X-ray powder diffraction (XRPD), where $\text{CuK}\alpha$ radiation was used.

The microwave dielectric properties were investigated using the Hakki and Coleman method, by which a cylindrical sample is positioned between two copper plates. The microwave signal from the sample was investigated using a network analyzer (8720ES; Agilent Technologies, Inc.). The dielectric constant (ϵ_r) was calculated using the TE_{011} resonant mode [8]. The temperature coefficient of the resonator frequency (τ_f) was investigated at temperatures of 20–80 °C.

3 Results and discussion

3.1 Prepared Mg_2SiO_4 porous ceramics

The total porosity of the prepared porous samples decreased with increasing sintering temperature. For example, the case of the porous sample obtained by adding 50 wt% PMMA with pore diameter of 1.5 μm is depicted in Fig. 2(a).

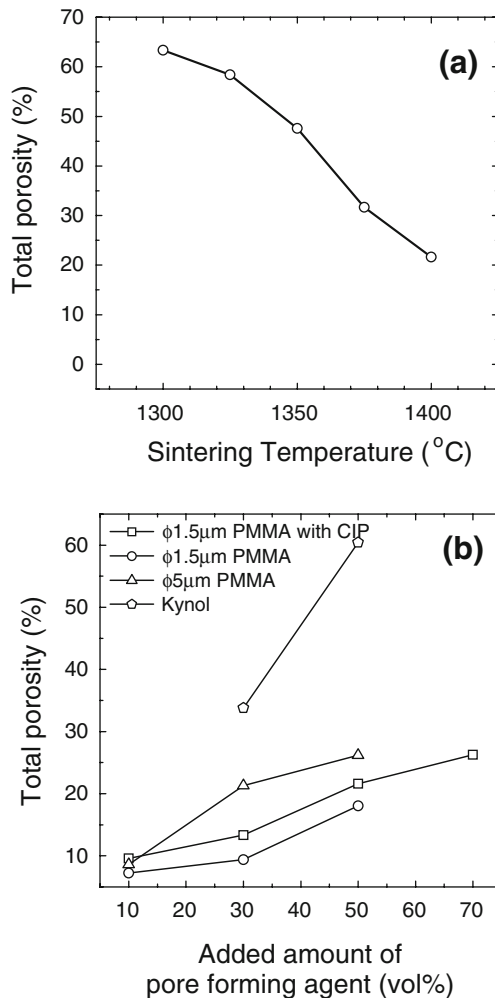


Fig. 2 (a) Total porosity vs. sintering temperature, where the 50 wt% PMMA of 1.5 μm was used as the pore-forming agent. (b) Total porosity vs. added amounts of pore-forming agents

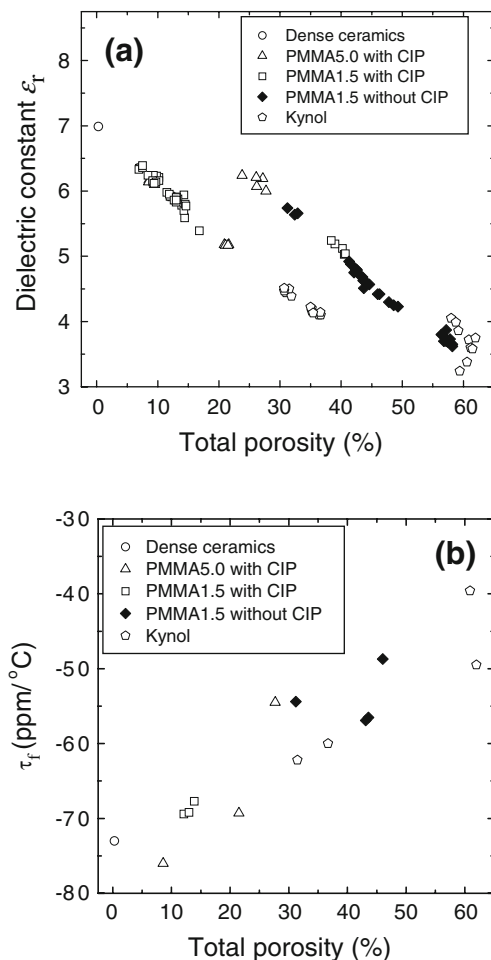


Fig. 3 (a) Dielectric constant (ϵ_r) and (b) temperature-dependence of resonant frequency (τ_f) of the prepared Mg_2SiO_4 porous ceramics vs. total porosity

The relations between total porosity and amount of the added pore-forming agent are shown in Fig. 2(b). The total porosity increased monotonously with amounts of each pore-forming agent. For equal amounts of each pore-forming agent, the total porosity indicated a different value for each pore-forming agent. The results showed that its total porosity depended also on the size of the pore-forming agent. Larger pore-forming agents tended to show higher total porosity. Consequently, the total porosities were determined using the sintering temperature, the kind of pore-forming agent, and the added amount of the agent.

The ϵ_r values of the Mg_2SiO_4 porous ceramics prepared in various conditions are presented in Fig. 3(a). The ϵ_r decreased with higher total porosity of the porous samples, although it was presumably independent on the pore form or the pore size. That fact suggests that ϵ_r decreased with increase of the fraction of air characterized by the pores in the Mg_2SiO_4 porous ceramics because the ϵ_r of air is almost unity.

The values of τ_f of the Mg_2SiO_4 porous ceramics are shown in Fig. 3(b). The τ_f approached zero with higher total porosities, resulting from $\tau_f=0$ ppm/°C of the pores in the Mg_2SiO_4 porous ceramics.

The relation between Q_f and total porosity is shown in Fig. 4(a). The Q_f of Mg_2SiO_4 porous ceramics with total porosity of 9.6% was higher than that of Mg_2SiO_4 dense ceramics with total porosity of 0.3%. That fact suggests that the total porosity is an improper factor for Q_f . We infer that Q_f is more closely related to the open porosity. As portrayed in Fig. 4(b), Q_f decreased monotonously with increased open porosity in the low open porosity range up to about 10%. However, the origin of the Q_f becomes more complicated in the higher opened porosity range over about 10%. For example, Q_f of a porous sample with open porosity of 35% obtained by kynol was approximately ten times higher than that with the same open porosity obtained by 5 $\mu\text{m}\varphi$ PMMA, meaning that not only Q_f was affected by open porosities. We infer that the difference in the open pore form or the open pore size is related to variation of Q_f .

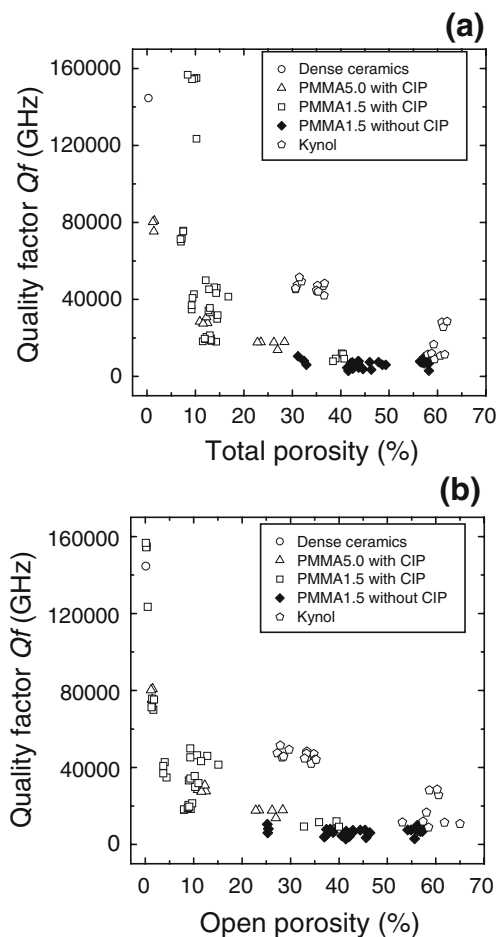


Fig. 4 Quality factor of the prepared Mg_2SiO_4 porous ceramics vs. (a) total porosity and (b) open porosity

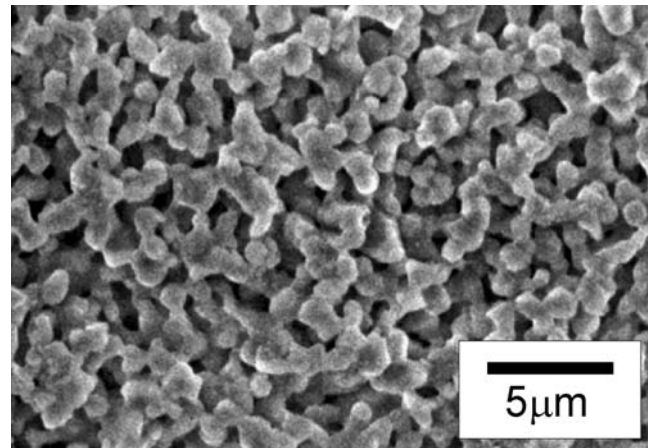


Fig. 5 Cross-sectional SEM image of the Mg_2SiO_4 porous ceramics with total porosity of 43.7% prepared with 50 vol.% 1.5 $\mu\text{m}\varphi$ PMMA

3.2 TiO_2 deposited Mg_2SiO_4 composite ceramics using LPD

We selected a porous sample with porosity of 43.7% obtained using 1.5 $\mu\text{m}\varphi$ PMMA to deposit TiO_2 in its pores. Figure 5 shows cross-sectional SEM images of the porous sample. First, the influence of the solution concentration on the deposition was investigated using the porous sample. As presented in Table 1, the amount of deposited TiO_2 increased with increasing concentration, indicating that the solutions of the 0.6 mol/l for $(\text{NH}_4)_2\text{TiF}_6$ and 1.2 mol/l for H_3BO_3 is appropriate for effective deposition.

Using the solutions of the 0.6 mol/l for $(\text{NH}_4)_2\text{TiF}_6$ and 1.2 mol/l for H_3BO_3 , we executed two LPD processes, as described in Section 2. The cross-sectional SEM views of porous Mg_2SiO_4 ceramics deposited with TiO_2 using two different LPD processes are depicted in Fig. 6(a) and (b), where (1) shows the outside part near the surface and (2) shows the inside. Compared to the inside, the outside image shows that TiO_2 is well deposited near the surface for each process. The deposited TiO_2 was also observed in the inside, but the deposited amount seems to be less than those of the outside. For process II, the amount of deposited TiO_2 was 3.5 wt%, which was 0.2% more than for process I

Table 1 Preparation conditions for deposition of TiO_2 in the Mg_2SiO_4 porous sample.

Sample	Deposition process	$(\text{NH}_4)_2\text{TiF}_6$ (mol/l)	H_3BO_3 (mol/l)	Deposited TiO_2 (wt%)
I-02	Process I	0.2	0.4	2.7
I-04	Process I	0.4	0.8	2.9
I-06	Process I	0.6	1.2	3.3
II-06	Process II	0.6	1.2	3.5

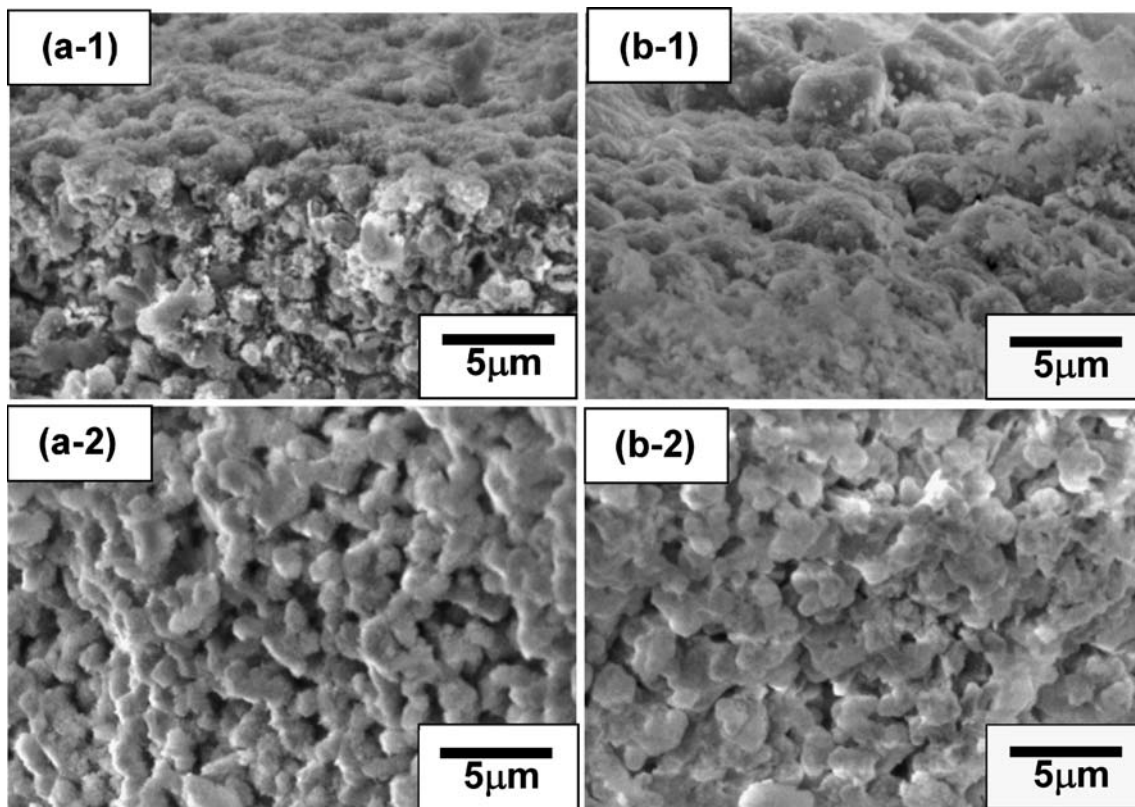


Fig. 6 Cross-sectional SEM images of the TiO_2 deposited Mg_2SiO_4 samples prepared using (a) process I and (b) process II, where (1) shows the outside part near the surface and (2) inside

(Table 1). Results show that LPD process II was more advantageous than LPD process I for deposition of TiO_2 . However, it was difficult to insert TiO_2 into all pores; that remains as a challenge for future study.

The XRPD patterns of the prepared TiO_2 deposited Mg_2SiO_4 are portrayed in Fig. 7(a)–(c), where Fig. 7(b) and (c) are magnified versions of Fig. 7(a). The reflections from TiO_2 showed an almost anatase form, not rutile (Fig. 7(a) and (b)). The peak intensity was smaller and the line width was broader than those of the Mg_2SiO_4 phase, indicating that crystallinity of the deposited anatase TiO_2 was lower. In addition, small reflections of secondary phases, MgSiO_3 and MgTiO_3 were also observed, indicating that the sintering temperature of 700°C is high for preventing the reaction between TiO_2 and Mg_2SiO_4 . The intensities of the secondary phases were highest for sample II-06, resulting from the largest TiO_2 deposited amount.

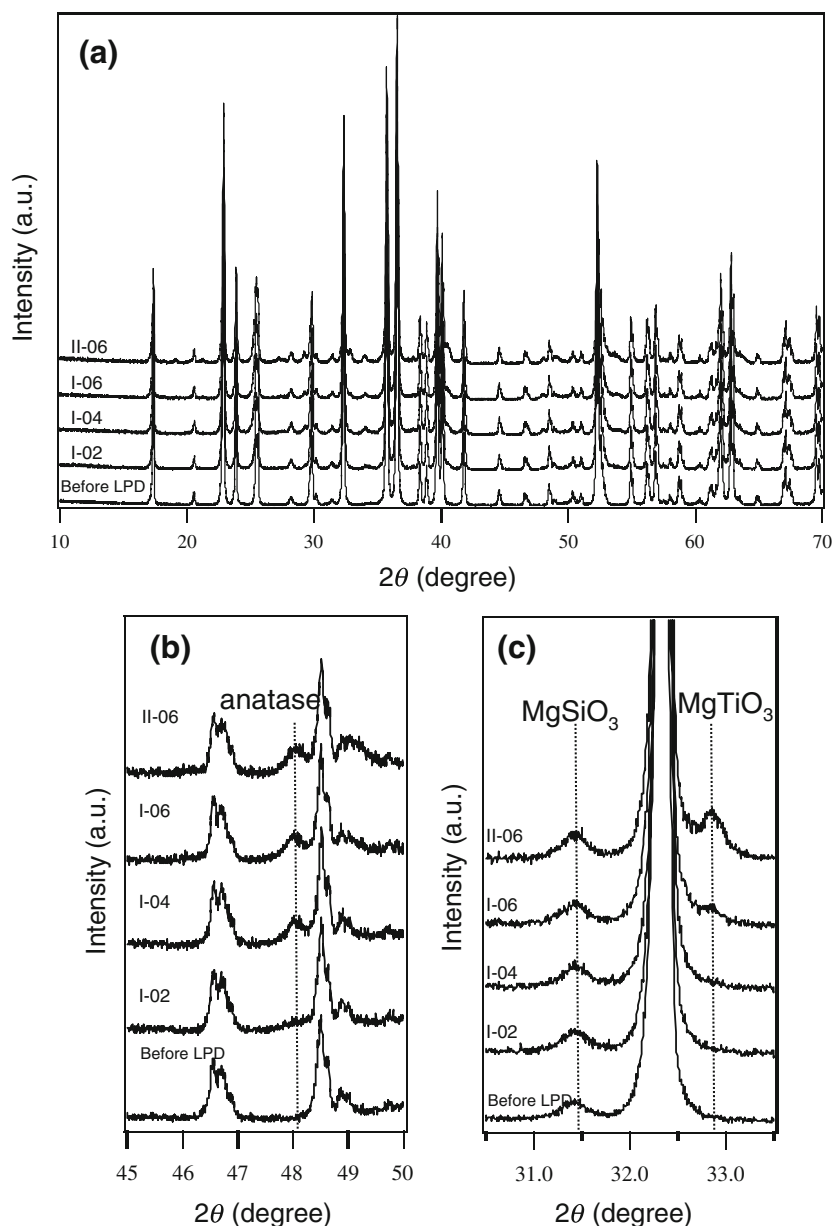
Microwave dielectric properties of the TiO_2 deposited sample were compared to those of the non-deposited one in Table 2. The value of ϵ_r increased as the amount of TiO_2 increased because of higher ϵ_r of the deposited TiO_2 . Samples with a larger amount of TiO_2 tended to approach 0. However, Qf becomes smaller than that of the non-deposited samples because of the low crystallinity of the TiO_2 and presence of the secondary phase.

We investigated another porous sample with porosity of 59.6% obtained by kynol pore-forming agents. The TiO_2 deposited amount and its microwave dielectric properties are presented in Table 3. The deposited TiO_2 amount was greater than that of sample obtained using the PMMA because of larger open porosities. In addition, τ_f improved from -40 to -5 ppm/ $^\circ\text{C}$ when the LPD process II was conducted. However, the Qf value decreased to 3400. To maintain a higher Qf value for TiO_2 deposited Mg_2SiO_4 , we must investigate a condition for fine crystallinity of TiO_2 ; that will be studied in future work.

4 Conclusions

We prepared porous Mg_2SiO_4 samples with various porosities using PMMA and kynol as pore-forming agents. We then inserted TiO_2 into the pores of the porous Mg_2SiO_4 using LPD. The TiO_2 was deposited in pores as anatase form. Microwave dielectric properties of the Mg_2SiO_4 porous ceramics and the TiO_2 deposited Mg_2SiO_4 were investigated. The ϵ_r or absolute value of τ_f of the Mg_2SiO_4 porous ceramics decreased with higher total porosity of the porous samples, although it was presumably independent of the pore form and pore size. The Qf of the Mg_2SiO_4 porous

Fig. 7 (a) XRPD pattern of the TiO_2 deposited Mg_2SiO_4 samples in the full 2θ range. (b), (c) the magnified XRPD pattern of (a). It is noteworthy that I-02, I-04, I-06, and II-6 are the prepared samples listed in Table 1



ceramics was more closely related to the open porosity rather than to the total porosity. With TiO_2 deposition in Mg_2SiO_4 porous ceramics, ϵ_r increased concomitant with the amount of TiO_2 because of higher ϵ_r of the TiO_2 . The Mg_2SiO_4 with

a larger amount of TiO_2 tended to approach 0. However, the Qf becomes smaller than that of the non-deposited samples. The value of τ_f of -5 ppm/ $^\circ\text{C}$ was achieved when 16.9 wt% TiO_2 was deposited in the Mg_2SiO_4 porous sample with total

Table 2 Microwave dielectric properties of TiO_2 deposited Mg_2SiO_4 prepared using Processes I and II, where the porous Mg_2SiO_4 shown in Fig. 5 was used.

Deposition process	Deposited TiO_2 (wt%)	ϵ_r	Qf (GHz)	τ_f (ppm/ $^\circ\text{C}$)	
I	Before LPD	–	4.6	7839	–57
	After LPD	3.3	4.9	6651	–50
II	Before LPD	–	4.5	4586	–57
	After LPD	3.5	4.7	4875	–49

Table 3 Microwave dielectric properties of TiO_2 deposited Mg_2SiO_4 prepared using processes I and II, where the used porous Mg_2SiO_4 with porosity of 59.6% was prepared using 50 vol.% kynol.

Deposition process	Deposited TiO_2 (wt%)	ϵ_r	Qf (GHz)	τ_f (ppm/ $^\circ\text{C}$)	
I	Before LPD	–	4.0	11900	–40
	After LPD	5.2	4.2	4200	–19
II	Before LPD	–	4.0	11458	–40
	After LPD	16.9	5.0	3416	–5

porosity of 59.6%, as obtained using kynol as the pore-forming agent.

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