

# Synthesis and Microwave Dielectric Properties of MgO–TiO<sub>2</sub>–SiO<sub>2</sub> Ceramics

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**Abstract**—The dielectric properties of MgO–TiO<sub>2</sub>–SiO<sub>2</sub> ceramics were studied. The results demonstrate that the presence of MgTi<sub>2</sub>O<sub>5</sub> increases dielectric losses in the ceramics. The synthesized materials offer low microwave losses and temperature-stable permittivity in the range 10–20.

## INTRODUCTION

Advances in wireless applications are highly dependent on the development of new low-loss (high  $Q = 1/\tan\delta$ ) microwave materials [1–3]. Availability of high- $Q$  ( $Qf \approx 10^5$  GHz) dielectrics with temperature coefficients of permittivity ( $TCP = \frac{1}{\epsilon} \frac{\partial \epsilon}{\partial T}$ ) on the order

of  $10^{-6}$  K<sup>-1</sup> is critical for GHz applications. Considerable research effort has been recently concentrated on the development of temperature-stable high- $Q$  dielectrics with permittivity in the range 10 to 20 [4, 5]. The use of such materials in filters and generators for communication systems offers the possibility of enhancing their sensitivity and selectivity [6, 7].

High- $Q$  dielectrics with  $\epsilon = 10$ –20 can be prepared using MgO–SiO<sub>2</sub> and MgO–TiO<sub>2</sub> oxides [8, 9]. The compounds existing in these systems include magnesium meta- and orthosilicates (MgSiO<sub>3</sub>, Mg<sub>2</sub>SiO<sub>4</sub>), magnesium meta- and orthotitanates (MgTiO<sub>3</sub>, Mg<sub>2</sub>TiO<sub>4</sub>), and magnesium dititanate (MgTi<sub>2</sub>O<sub>5</sub>).

Materials based on Mg<sub>2</sub>SiO<sub>4</sub>, MgTiO<sub>3</sub>, and Mg<sub>2</sub>TiO<sub>4</sub> are considered potentially attractive for designing low-TCP microwave dielectrics [6–9]. Available data on their microwave dielectric losses are however contradictory. For example, the  $Qf$  values reported for MgTiO<sub>3</sub>-based materials range from  $3 \times 10^4$  to  $10^5$  GHz [7–9], indicating that the chemical composition of the material and synthesis conditions have a significant effect on its microwave losses.

There are also problems arising from the high (>1500°C) sintering temperatures of polycrystalline materials based on magnesium titanates and silicates. To obviate this difficulty, use has been made of various additives and fluxes [8–10]. It is reasonable to expect that a viable approach to the fabrication of dense

ceramics at relatively low (<1400°C) sintering temperatures is the use of multicomponent magnesium silicate and titanate systems. Moreover, since the dielectric permittivity of Mg<sub>2</sub>SiO<sub>4</sub> is 6.5 [10] and those of MgTiO<sub>3</sub> and Mg<sub>2</sub>TiO<sub>4</sub> are 16 and 14, respectively [10], one can engineer controlled-permittivity materials by tuning the phase composition of the system.

The objective of this work was to prepare low-loss, low-TCP microwave ceramics based on compounds of the MgO–TiO<sub>2</sub>–SiO<sub>2</sub> system. To this end, we examined the effects of starting-mixture composition and heat-treatment temperature on the phase composition of  $(1-x)\text{Mg}_2\text{SiO}_4-x\text{MgTiO}_3$  and  $(1-x)\text{Mg}_2\text{SiO}_4-x\text{Mg}_2\text{TiO}_4$  ( $x = 0, 0.25, 0.5, 0.75, 1$ ) ceramics and also the effect of phase composition on the dielectric properties of the ceramics.

## EXPERIMENTAL

Samples for this investigation were prepared by solid-state reactions, using analytical-grade MgO and MgCO<sub>3</sub> and extrapure-grade SiO<sub>2</sub> and TiO<sub>2</sub>. The starting mixtures were homogenized by ball milling with bidistilled water. After evaporating the residual water, the mixtures were dried at 100–150°C, passed through a nylon-6 sieve, and pressed at 50 MPa into pellets, which were then fired at 600–1400°C. After heat treatment, the samples were ground, and their phase compositions were determined by x-ray diffraction (XRD) on a DRON-3M powder diffractometer (CuK $\alpha$  radiation, step-scan mode with a step size  $\Delta 2\theta = 0.02^\circ$  and a counting time per data point of 10 s). As external standards, we used SiO<sub>2</sub> (2 $\theta$  calibration) and Al<sub>2</sub>O<sub>3</sub> (NIST SRM1976 intensity standard). In phase analysis, we used JCPDS Powder Diffraction File data.

Mg<sub>2</sub>SiO<sub>4</sub>, MgTiO<sub>3</sub>, and Mg<sub>2</sub>TiO<sub>4</sub> were prepared by reacting appropriate mixtures at 1150–1200°C for 2 h. To obtain ceramic samples, the synthesized materials were pressed into pellets 10 mm in diameter and 3–4 mm in thickness and sintered at  $t_{\text{sint}} = 1300\text{--}1400^\circ\text{C}$  for 2 h. Microwave measurements were performed at 10 GHz using the dielectric-resonator method [11–13].

## RESULTS AND DISCUSSION

To optimize the synthesis temperatures for Mg<sub>2</sub>SiO<sub>4</sub>, MgTiO<sub>3</sub>, and Mg<sub>2</sub>TiO<sub>4</sub>, we examined the phase changes involved in the formation of these compounds. XRD results indicated that, irrespective of whether MgO or MgCO<sub>3</sub> was used as the Mg precursor, the formation of Mg<sub>2</sub>SiO<sub>4</sub> began at 1000°C (Fig. 1). With both precursors, the samples synthesized at 1150–1200°C contained trace levels of additional phases: MgSiO<sub>3</sub> (protoenstatite) and MgO. In the case of MgO, however, the percentages of these phases were substantially smaller (Fig. 1, scan 2). Note that protoenstatite transforms into clinoenstatite at  $t \geq 1200^\circ\text{C}$ . At heat-treatment temperatures above 1300°C, we obtained phase-pure Mg<sub>2</sub>SiO<sub>4</sub> (Fig. 1, scan 3).

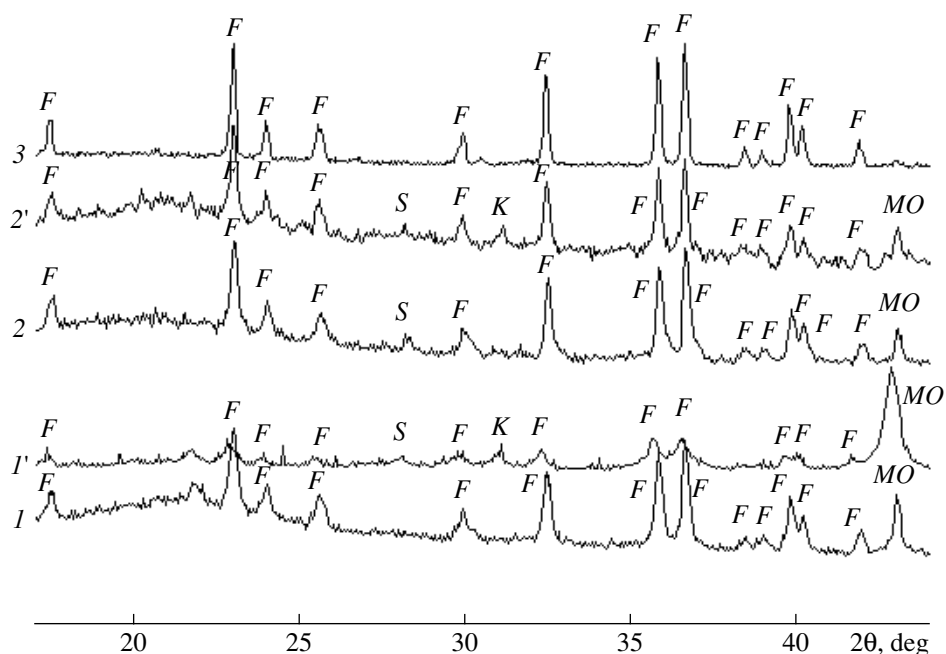
The formation of MgTiO<sub>3</sub> from equimolar mixtures of MgO and TiO<sub>2</sub> occurred in the range 800–1000°C. Heat treatment above 1000°C led to the formation of phase-pure MgTiO<sub>3</sub> (Fig. 2, scan 2). In the range 1300–1400°C (sintering temperatures), a small amount of MgTiO<sub>3</sub> decomposed to form Mg<sub>2</sub>TiO<sub>4</sub> (Fig. 2, scan 3).

The formation of Mg<sub>2</sub>TiO<sub>4</sub> required higher temperatures in comparison with MgTiO<sub>3</sub>. The material prepared by reacting a 2MgO + TiO<sub>2</sub> mixture at 1000°C contained not only Mg<sub>2</sub>TiO<sub>4</sub> but also MgTiO<sub>3</sub>, TiO<sub>2</sub>, MgO, and a small amount of MgTi<sub>2</sub>O<sub>5</sub>, resulting from the reaction between MgTiO<sub>3</sub> and TiO<sub>2</sub> (Fig. 3, scan 1). At 1200–1300°C, the MgTiO<sub>3</sub> and MgO reacted to form Mg<sub>2</sub>TiO<sub>4</sub> (Fig. 3, scan 2). Phase-pure Mg<sub>2</sub>TiO<sub>4</sub> was obtained in the range 1300–1400°C (sintering temperatures) (Fig. 3, scan 3).

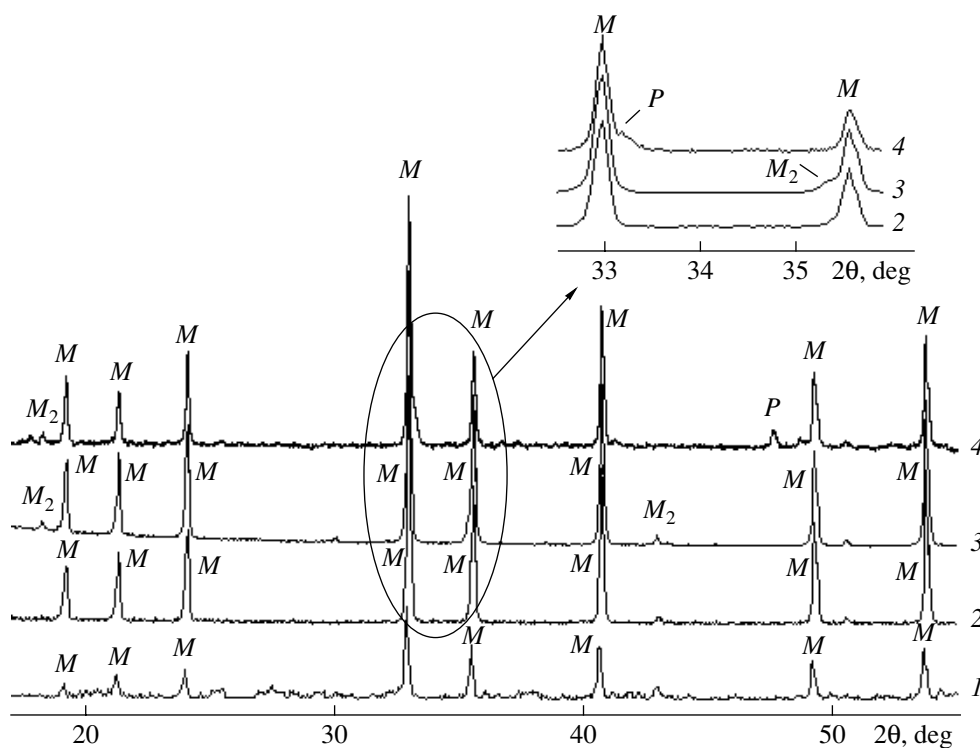
XRD results for  $(1 - x)\text{Mg}_2\text{SiO}_4 - x\text{Mg}_2\text{TiO}_4$  ( $x = 0.25, 0.5, 0.75$ ) samples indicated that no reaction took place at 1350°C (Fig. 4). Independent of  $x$ , the only phases present were Mg<sub>2</sub>SiO<sub>4</sub> and Mg<sub>2</sub>TiO<sub>4</sub>.

XRD examination of  $(1 - x)\text{Mg}_2\text{SiO}_4 - x\text{MgTiO}_3$  samples indicated the presence of Mg<sub>2</sub>SiO<sub>4</sub>, MgTiO<sub>3</sub>, and MgTi<sub>2</sub>O<sub>5</sub> (Fig. 5). At  $x < 0.25$ , no MgTi<sub>2</sub>O<sub>5</sub> was detected.

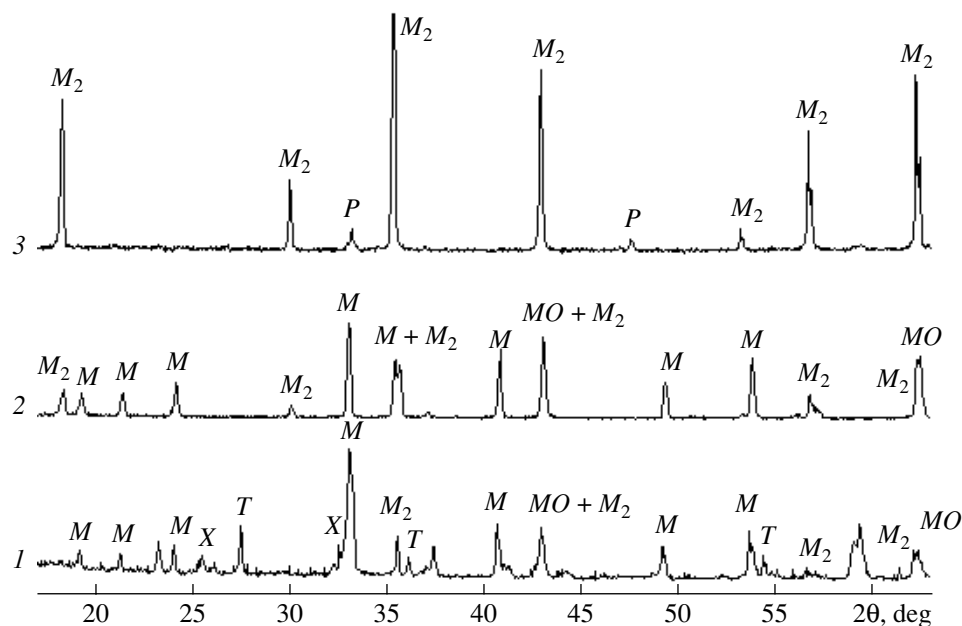
Dielectric measurements showed that the synthesized Mg<sub>2</sub>SiO<sub>4</sub>, MgTiO<sub>3</sub>, and Mg<sub>2</sub>TiO<sub>4</sub> had positive TCP, in the range  $(50\text{--}100) \times 10^{-6} \text{ K}^{-1}$ , whereas microwave applications require materials with TCP within the range  $\pm 10 \times 10^{-6} \text{ K}^{-1}$ . One way of preparing low-TCP materials based on the compounds in question is by adding a negative-TCP phase to ensure permittivity thermocompensation [3]. Moreover, such additives must be nonreactive with the other components of the material. As a negative-TCP additive, we used CaTiO<sub>3</sub> (perovskite), which is known to have  $\text{TCP} = -900 \times 10^{-6} \text{ K}^{-1}$  [3, 8–10]. Since this compound has high dielectric permittivity (on the order of 160), even



**Fig. 1.** XRD patterns of samples prepared by reacting  $(1\text{--}3)$   $2\text{MgO} + \text{SiO}_2$  and  $(1', 2')$   $2\text{MgCO}_3 + \text{SiO}_2$  mixtures at  $(1, 1')$  1000,  $(2, 2')$  1200, and  $(3)$  1350°C;  $F = \text{Mg}_2\text{SiO}_4$ ,  $S = \text{MgSiO}_3$  (protoenstatite),  $K = \text{MgSiO}_3$  (clinoenstatite),  $MO = \text{MgO}$ .



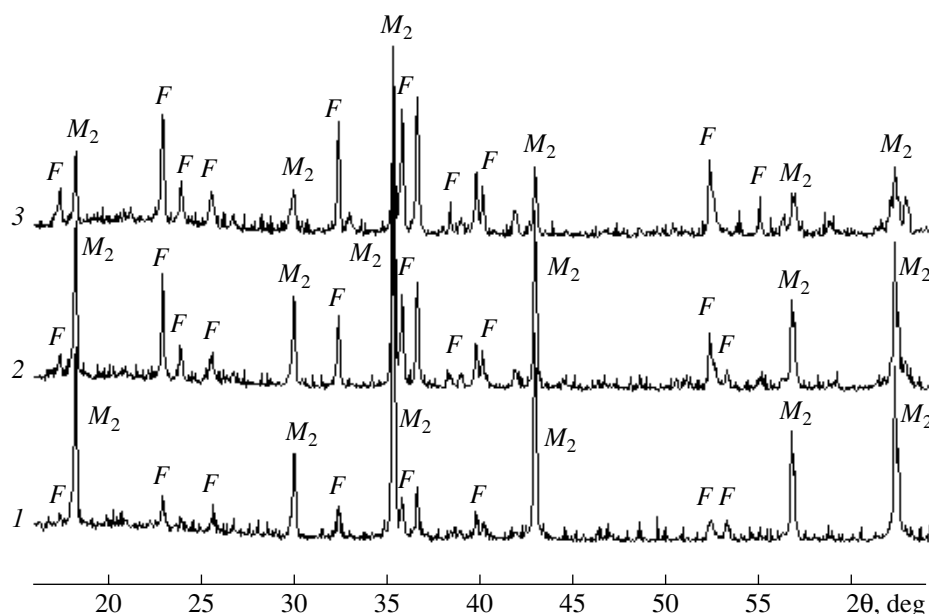
**Fig. 2.** XRD patterns of samples prepared by reacting  $\text{MgO} + \text{TiO}_2$  mixtures at (1) 1000, (2) 1200, and (3, 4) 1350°C; (4) mixture containing 8 mol %  $\text{CaTiO}_3$  additions;  $M_2 = \text{Mg}_2\text{TiO}_4$ ,  $P = \text{CaTiO}_3$ ,  $M = \text{MgTiO}_3$ . Inset: strongest reflections from  $\text{Mg}_2\text{TiO}_4$  and  $\text{CaTiO}_3$ .



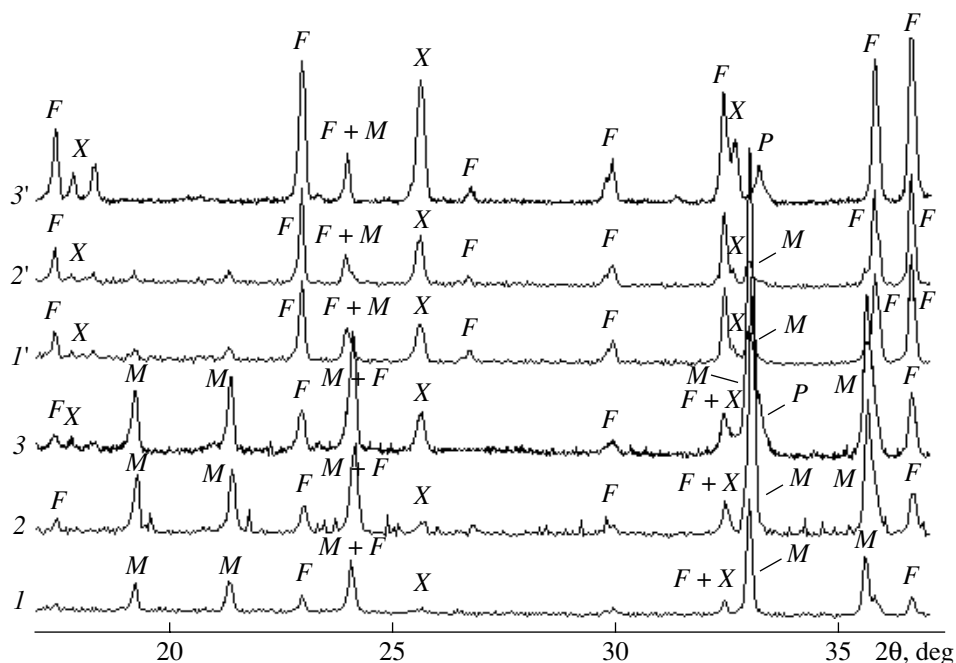
**Fig. 3.** XRD patterns of samples prepared by reacting  $2\text{MgO} + \text{TiO}_2$  mixtures at (1) 1000, (2) 1200, and (3) 1350°C; (3) mixture containing 2 mol %  $\text{CaO}$  additions;  $M_2 = \text{Mg}_2\text{TiO}_4$ ,  $P = \text{CaTiO}_3$ ,  $M = \text{MgTiO}_3$ ,  $MO = \text{MgO}$ ,  $T = \text{TiO}_2$ .

small  $\text{CaTiO}_3$  additions may increase the permittivity of the materials in question to 10–20, which is of practical importance in a number of engineering applications [4–7].

Table 1 summarizes our results for a number of low-TCP materials based on  $\text{MgO-TiO}_2\text{-SiO}_2$ .  $\text{CaTiO}_3$  additions are seen to ensure efficient permittivity thermocompensation and to reduce the sintering tempera-



**Fig. 4.** XRD patterns of polycrystalline  $(1-x)\text{Mg}_2\text{SiO}_4-x\text{Mg}_2\text{TiO}_4$  samples sintered at 1350°C:  $x = (1) 0.75, (2) 0.5, (3) 0.25$ ;  $F = \text{Mg}_2\text{SiO}_4, M_2 = \text{Mg}_2\text{TiO}_4$ .



**Fig. 5.** XRD patterns of polycrystalline  $(1-x)\text{Mg}_2\text{SiO}_4-x\text{MgTiO}_3$  samples heat-treated at  $(1, 1') 1000$  and  $(2, 2', 3, 3') 1350^\circ\text{C}$ ;  $x = (1-3) 0.75, (1'-3') 0.25$ ;  $(3, 3')$  mixture containing 6 mol %  $\text{CaTiO}_3$ ;  $F = \text{Mg}_2\text{SiO}_4, M = \text{Mg}_2\text{TiO}_4, X = \text{MgTi}_2\text{O}_5, P = \text{CaTiO}_3$ .

ture by 50–100°C. The materials possess good temperature stability of permittivity, low dielectric losses, and  $\epsilon$  in the range 15–25.

The dielectric properties of composites based on  $(1-x)\text{Mg}_2\text{SiO}_4-x\text{Mg}_2\text{TiO}_4$  and  $(1-x)\text{Mg}_2\text{SiO}_4-x\text{MgTiO}_3$  are summarized in Table 2. These results

demonstrate that we obtained low-microwave-loss materials with permittivities in the range 10–20, depending on the phase composition of the ceramics. Note that the presence of  $\text{MgTi}_2\text{O}_5$  markedly raises (by a factor of 2–3) dielectric losses in the ceramics (Table 2). The MgO–TiO<sub>2</sub>–SiO<sub>2</sub> composites feature low sintering

**Table 1.** 10-GHz dielectric properties and phase composition of materials based on MgO–TiO<sub>2</sub>–SiO<sub>2</sub>

| Starting mixture                                           | $t_{\text{sint}}, ^\circ\text{C}$ | $\epsilon$ | $\text{TCP} \times 10^6, \text{K}^{-1}$ | $Q = 1/\tan\delta$ | Phase composition                                                                             |
|------------------------------------------------------------|-----------------------------------|------------|-----------------------------------------|--------------------|-----------------------------------------------------------------------------------------------|
| Mg <sub>2</sub> TiO <sub>4</sub> + 0.05 CaTiO <sub>3</sub> | 1450                              | 22         | +8                                      | 4000               | Mg <sub>2</sub> TiO <sub>4</sub> , CaTiO <sub>3</sub>                                         |
| MgTiO <sub>3</sub> + 0.05 CaTiO <sub>3</sub>               | 1400                              | 20         | –5                                      | 5000               | MgTiO <sub>3</sub> , CaTiO <sub>3</sub>                                                       |
| Mg <sub>2</sub> SiO <sub>4</sub> + 0.1 CaTiO <sub>3</sub>  | 1450                              | 12         | +20                                     | 3500               | Mg <sub>2</sub> SiO <sub>4</sub> , CaTiO <sub>3</sub>                                         |
| MgTi <sub>2</sub> O <sub>5</sub> + 0.06 CaTiO <sub>3</sub> | 1350                              | 30         | +30                                     | 1000               | MgTi <sub>2</sub> O <sub>5</sub> , MgTiO <sub>3</sub> , TiO <sub>2</sub> , CaTiO <sub>3</sub> |

**Table 2.** 10-GHz dielectric properties and phase composition of composites based on (1 – x)Mg<sub>2</sub>SiO<sub>4</sub>–xMgTiO<sub>3</sub> and (1 – x)Mg<sub>2</sub>SiO<sub>4</sub>–xMg<sub>2</sub>TiO<sub>4</sub>

| Starting mixture                                                                                        | $t_{\text{sint}}, ^\circ\text{C}$ | $\epsilon$ | $\text{TCP} \times 10^6, \text{K}^{-1}$ | $Q = 1/\tan\delta$ | Phase composition                                                                                             |
|---------------------------------------------------------------------------------------------------------|-----------------------------------|------------|-----------------------------------------|--------------------|---------------------------------------------------------------------------------------------------------------|
| 0.75 Mg <sub>2</sub> SiO <sub>4</sub> + 0.25 MgTiO <sub>3</sub> + 0.06 CaTiO <sub>3</sub>               | 1380                              | 10         | –5                                      | 1800               | Mg <sub>2</sub> SiO <sub>4</sub> , MgTi <sub>2</sub> O <sub>5</sub> , MgTiO <sub>3</sub> , CaTiO <sub>3</sub> |
| 0.5 Mg <sub>2</sub> SiO <sub>4</sub> + 0.5 MgTiO <sub>3</sub> + 0.06 CaTiO <sub>3</sub>                 | 1380                              | 12         | +5                                      | 4000               | Mg <sub>2</sub> SiO <sub>4</sub> , MgTiO <sub>3</sub> , MgTi <sub>2</sub> O <sub>5</sub> , CaTiO <sub>3</sub> |
| 0.75 Mg <sub>2</sub> SiO <sub>4</sub> + 0.25 MgTiO <sub>3</sub> + 0.06 CaTiO <sub>3</sub>               | 1350                              | 15         | –8                                      | 5000               | Mg <sub>2</sub> SiO <sub>4</sub> , MgTiO <sub>3</sub> , MgTi <sub>2</sub> O <sub>5</sub> , CaTiO <sub>3</sub> |
| 0.5 Mg <sub>2</sub> SiO <sub>4</sub> + 0.5 MgTiO <sub>3</sub> + 0.1 CaTiO <sub>3</sub>                  | 1370                              | 12.5       | +15                                     | 3000               | MgTiO <sub>3</sub> , MgTi <sub>2</sub> O <sub>5</sub> , Mg <sub>2</sub> SiO <sub>4</sub> , CaTiO <sub>3</sub> |
| 0.25 Mg <sub>2</sub> SiO <sub>4</sub> + 0.75 Mg <sub>2</sub> TiO <sub>4</sub> + 0.06 CaTiO <sub>3</sub> | 1400                              | 14.5       | –10                                     | 4000               | Mg <sub>2</sub> SiO <sub>4</sub> , Mg <sub>2</sub> TiO <sub>4</sub> , CaTiO <sub>3</sub>                      |
| 0.5 Mg <sub>2</sub> SiO <sub>4</sub> + 0.5 Mg <sub>2</sub> TiO <sub>4</sub> + 0.06 CaTiO <sub>3</sub>   | 1400                              | 12.5       | –5                                      | 3000               | Mg <sub>2</sub> TiO <sub>4</sub> , Mg <sub>2</sub> SiO <sub>4</sub> , CaTiO <sub>3</sub>                      |

temperatures (<1400°C), high temperature stability of properties (owing to the effective thermocompensation upon the introduction of small CaTiO<sub>3</sub> additions), and low dielectric losses. They are potentially attractive for various electronic applications.

## CONCLUSIONS

We studied chemical interactions of Mg<sub>2</sub>SiO<sub>4</sub> with Mg<sub>2</sub>TiO<sub>4</sub> and MgTiO<sub>3</sub> and identified conditions under which the MgTi<sub>2</sub>O<sub>5</sub> phase (having an adverse effect on microwave losses) is formed in the MgO–TiO<sub>2</sub>–SiO<sub>2</sub> system. Our results demonstrate that CaTiO<sub>3</sub> additions reduce the sintering temperature of the ceramics studied by 50–100°C and ensure efficient permittivity thermocompensation. The synthesized materials offer low microwave losses and dielectric permittivities in the range 10–20.

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