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Synthesis and Microwave Dielectric Properties of $MgO–TiO_2–SiO_2$ Ceramics

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Abstract—The dielectric properties of $MgO–TiO_2–SiO_2$ ceramics were studied. The results demonstrate that the presence of $MgTi_2O_5$ 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 ($Qf \simeq 10^5$ GHz) dielectrics with temperature coefficients of permittivity (TCP = $\frac{1}{\varepsilon}\frac{\partial\varepsilon}{\partial T}$) on the order of 10^{-6} K^{-1} 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 ε = 10–20 can be prepared using $MgO–SiO_2$ and $MgO–TiO_2$ oxides [8, 9]. The compounds existing in these systems include magnesium meta- and orthosilicates ($MgSiO_3$, Mg_2SiO_4), magnesium meta- and orthotitanates ($MgTiO_3$, Mg_2TiO_4), and magnesium dititanate ($MgTi_2O_5$).

Materials based on Mg_2SiO_4, $MgTiO_3$, and Mg_2TiO_4 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 $MgTiO_3$-based materials range from 3×10^4 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_2SiO_4 is 6.5 [10] and those of $MgTiO_3$ and Mg_2TiO_4 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 $MgO–TiO_2–SiO_2$ system. To this end, we examined the effects of starting-mixture composition and heat-treatment temperature on the phase composition of $(1 – x)Mg_2SiO_4–xMgTiO_3$ and $(1 – x)Mg_2SiO_4–xMg_2TiO_4$ (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 $MgCO_3$ and extrapure-grade SiO_2 and TiO_2. 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_α radiation, step-scan mode with a step size $\Delta 2\theta = 0.02°$ and a counting time per data point of 10 s). As external standards, we used SiO_2 (2θ calibration) and Al_2O_3 (NIST SRM1976 intensity standard). In phase analysis, we used JCPDS Powder Diffraction File data.

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Mg_2SiO_4, $MgTiO_3$, and Mg_2TiO_4 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_{sint} = 1300–1400°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_2SiO_4, $MgTiO_3$, and Mg_2TiO_4, we examined the phase changes involved in the formation of these compounds. XRD results indicated that, irrespective of whether MgO or $MgCO_3$ was used as the Mg precursor, the formation of Mg_2SiO_4 began at 1000°C (Fig. 1). With both precursors, the samples synthesized at 1150–1200°C contained trace levels of additional phases: $MgSiO_3$ (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 $t \geq 1200$°C. At heat-treatment temperatures above 1300°C, we obtained phase-pure Mg_2SiO_4 (Fig. 1, scan *3*).

The formation of $MgTiO_3$ from equimolar mixtures of MgO and TiO_2 occurred in the range 800–1000°C. Heat treatment above 1000°C led to the formation of phase-pure $MgTiO_3$ (Fig. 2, scan *2*). In the range 1300–1400°C (sintering temperatures), a small amount of $MgTiO_3$ decomposed to form Mg_2TiO_4 (Fig. 2, scan *3*).

The formation of Mg_2TiO_4 required higher temperatures in comparison with $MgTiO_3$. The material prepared by reacting a $2MgO + TiO_2$ mixture at 1000°C contained not only Mg_2TiO_4 but also $MgTiO_3$, TiO_2, MgO, and a small amount of $MgTi_2O_5$, resulting from the reaction between $MgTiO_3$ and TiO_2 (Fig. 3, scan *1*). At 1200–1300°C, the $MgTiO_3$ and MgO reacted to form Mg_2TiO_4 (Fig. 3, scan *2*). Phase-pure Mg_2TiO_4 was obtained in the range 1300–1400°C (sintering temperatures) (Fig. 3, scan *3*).

XRD results for $(1 - x)Mg_2SiO_4–xMg_2TiO_4$ (x = 0.25, 0.5, 0.75) samples indicated than no reaction took place at 1350°C (Fig. 4). Independent of x, the only phases present were Mg_2SiO_4 and Mg_2TiO_4.

XRD examination of $(1 - x)Mg_2SiO_4–xMgTiO_3$ samples indicated the presence of Mg_2SiO_4, $MgTiO_3$, and $MgTi_2O_5$ (Fig. 5). At $x < 0.25$, no $MgTi_2O_5$ was detected.

Dielectric measurements showed that the synthesized Mg_2SiO_4, $MgTiO_3$, and Mg_2TiO_4 had positive TCP, in the range $(50–100) \times 10^{-6}$ K^{-1}, whereas microwave applications require materials with TCP within the range $\pm 10 \times 10^{-6}$ 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 $CaTiO_3$ (perovskite), which is known to have TCP = -900×10^{-6} K^{-1} [3, 8–10]. Since this compound has high dielectric permittivity (on the order of 160), even

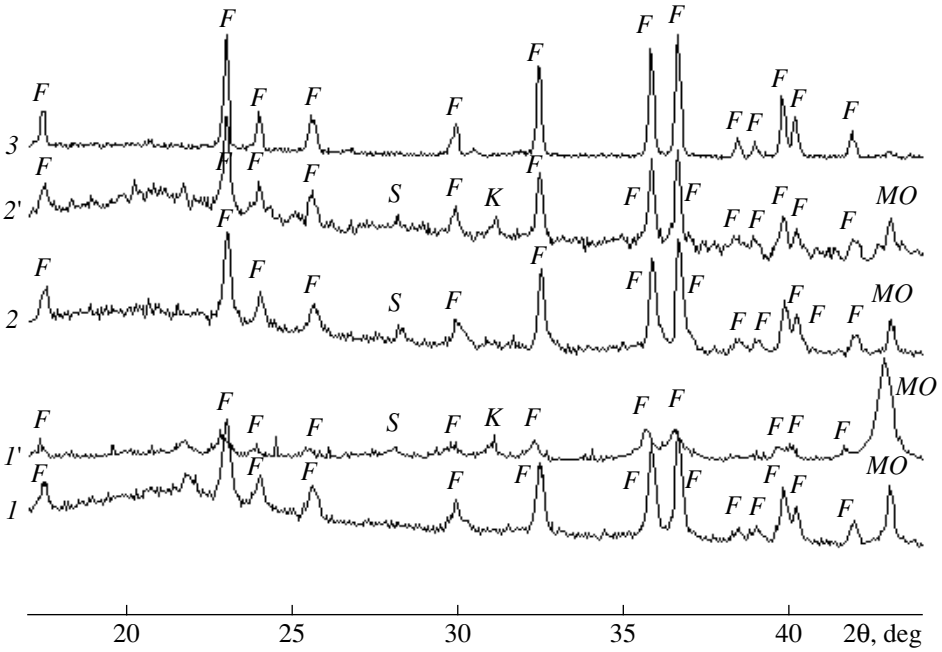

Fig. 1. XRD patterns of samples prepared by reacting (*1*–*3*) $2MgO + SiO_2$ and (*1*', *2*') $2MgCO_3 + SiO_2$ mixtures at (*1*, *1*') 1000, (*2*, *2*') 1200, and (*3*) 1350°C; $F = Mg_2SiO_4$, $S = MgSiO_3$ (protoenstatite), $K = MgSiO_3$ (clinoenstatite), MO = MgO.

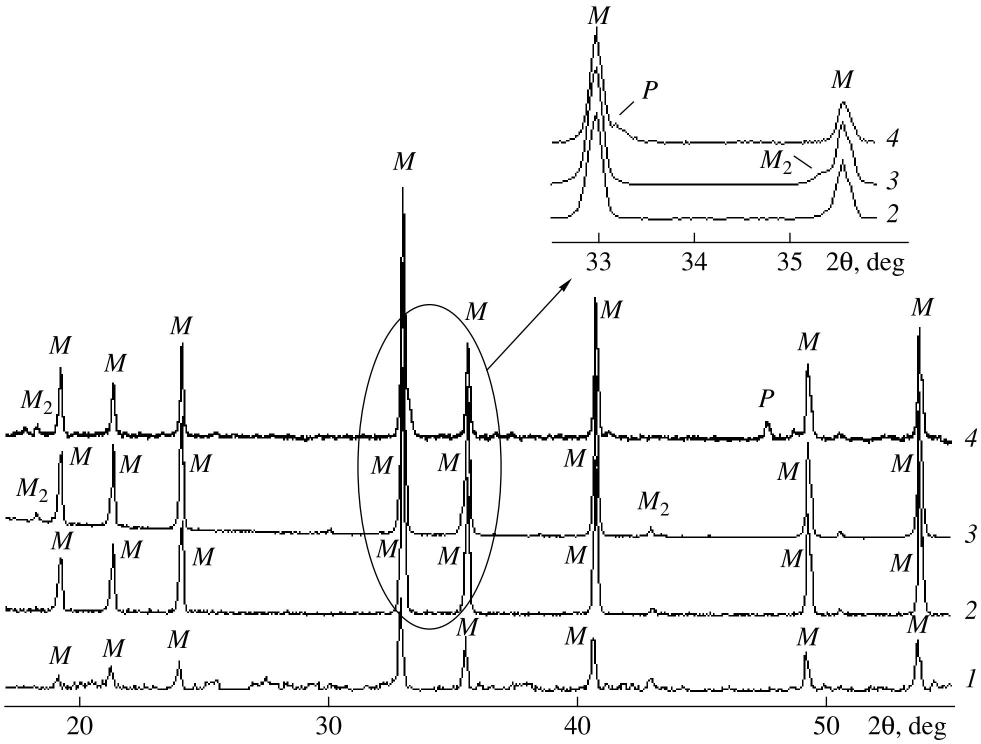

Fig. 2. XRD patterns of samples prepared by reacting MgO + TiO_2 mixtures at (*1*) 1000, (*2*) 1200, and (*3*, *4*) 1350°C; (*4*) mixture containing 8 mol % $CaTiO_3$ additions; M_2 = Mg_2TiO_4, *P* = $CaTiO_3$, *M* = $MgTiO_3$. Inset: strongest reflections from Mg_2TiO_4 and $CaTiO_3$.

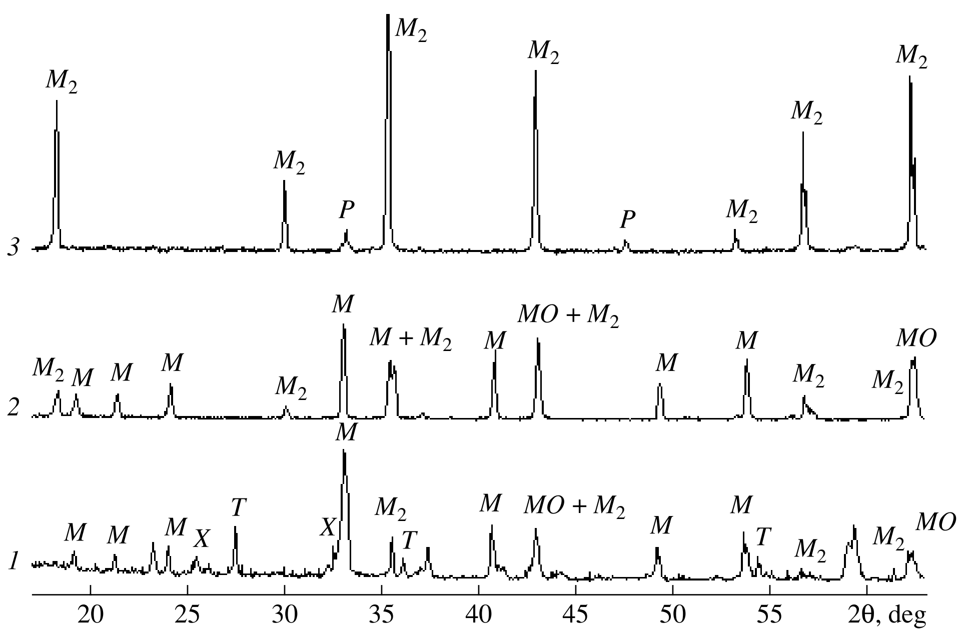

Fig. 3. XRD patterns of samples prepared by reacting 2MgO + TiO_2 mixtures at (*1*) 1000, (*2*) 1200, and (*3*) 1350°C; (*3*) mixture containing 2 mol % CaO additions; M_2 = Mg_2TiO_4, *P* = $CaTiO_3$, *M* = $MgTiO_3$, *MO* = MgO, *T* = TiO_2.

small $CaTiO_3$ 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 MgO–TiO_2–SiO_2. $CaTiO_3$ additions are seen to ensure efficient permittivity thermocompensation and to reduce the sintering tempera-

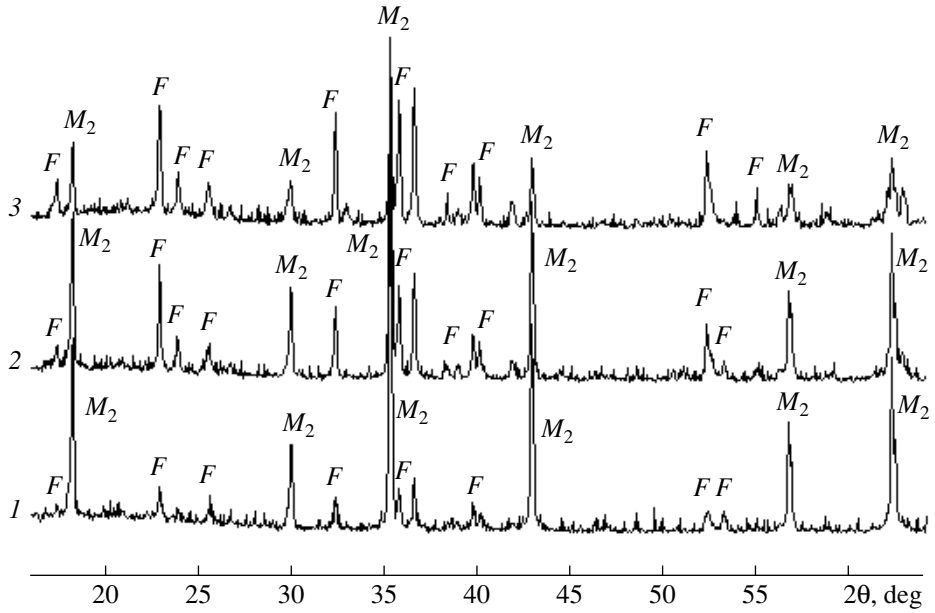

Fig. 4. XRD patterns of polycrystalline $(1 – x)Mg_2SiO_4–xMg_2TiO_4$samples sintered at 1350°C: x = (*1*) 0.75, (*2*) 0.5, (*3*) 0.25; $F = Mg_2SiO_4$, $M_2 = Mg_2TiO_4$.

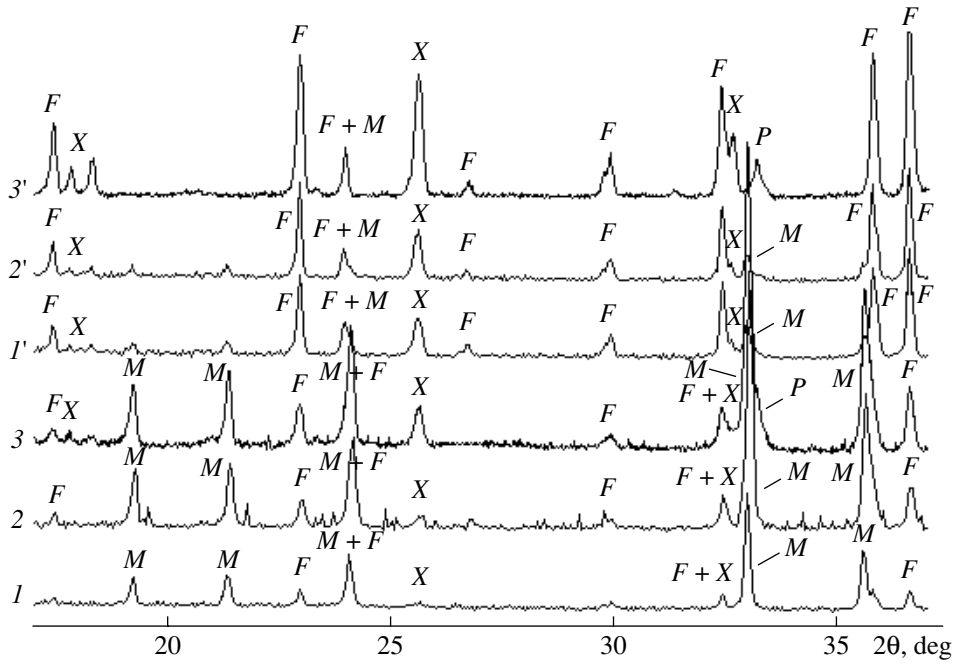

Fig. 5. XRD patterns of polycrystalline $(1 – x)Mg_2SiO_4–xMgTiO_3$ samples heat-treated at (*1*, *1*') 1000 and (*2*, *2*', *3*, *3*') 1350°C; x = (*1*–*3*) 0.75, (*1*'–*3*') 0.25; (*3*, *3*') mixture containing 6 mol % $CaTiO_3$; $F = Mg_2SiO_4$, $M = Mg_2TiO_4$, $X = MgTi_2O_5$, $P = CaTiO_3$.

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

The dielectric properties of composites based on $(1 – x)Mg_2SiO_4–xMg_2TiO_4$ and $(1 – x)Mg_2SiO_4–xMgTiO_3$ 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 $MgTi_2O_5$ markedly raises (by a factor of 2–3) dielectric losses in the ceramics (Table 2). The $MgO–TiO_2–SiO_2$ composites feature low sintering

Table 1. 10-GHz dielectric properties and phase composition of materials based on $MgO–TiO_2–SiO_2$

Starting mixture	t_{sint}, °C	ε	TCP × 10^6, K^{-1}	$Q = 1/\tan\delta$	Phase composition
Mg_2TiO_4 + 0.05 $CaTiO_3$	1450	22	+8	4000	Mg_2TiO_4, $CaTiO_3$
$MgTiO_3$ + 0.05 $CaTiO_3$	1400	20	–5	5000	$MgTiO_3$, $CaTiO_3$
Mg_2SiO_4 + 0.1 $CaTiO_3$	1450	12	+20	3500	Mg_2SiO_4, $CaTiO_3$
$MgTi_2O_5$ + 0.06 $CaTiO_3$	1350	30	+30	1000	$MgTi_2O_5$, $MgTiO_3$, TiO_2, $CaTiO_3$

Table 2. 10-GHz dielectric properties and phase composition of composites based on $(1 – x)Mg_2SiO_4–xMgTiO_3$ and $(1 – x)Mg_2SiO_4–xMg_2TiO_4$

Starting mixture	t_{sint}, °C	ε	TCP × 10^6, K^{-1}	$Q = 1/\tan\delta$	Phase composition
0.75 Mg_2SiO_4 + 0.25 $MgTiO_3$ + 0.06 $CaTiO_3$	1380	10	–5	1800	Mg_2SiO_4, $MgTi_2O_5$, $MgTiO_3$,$CaTiO_3$
0.5 Mg_2SiO_4 + 0.5 $MgTiO_3$ + 0.06 $CaTiO_3$	1380	12	+5	4000	Mg_2SiO_4, $MgTiO_3$, $MgTi_2O_5$, $CaTiO_3$
0.75 Mg_2SiO_4 + 0.25 $MgTiO_3$ + 0.06 $CaTiO_3$	1350	15	–8	5000	Mg_2SiO_4, $MgTiO_3$, $MgTi_2O_5$, $CaTiO_3$
0.5 Mg_2SiO_4 + 0.5 $MgTiO_3$ + 0.1 $CaTiO_3$	1370	12.5	+15	3000	$MgTiO_3$, $MgTi_2O_5$, Mg_2SiO_4, $CaTiO_3$
0.25 Mg_2SiO_4 + 0.75 Mg_2TiO_4 + 0.06 $CaTiO_3$	1400	14.5	–10	4000	Mg_2SiO_4, Mg_2TiO_4, $CaTiO_3$
0.5 Mg_2SiO_4 + 0.5 Mg_2TiO_4 + 0.06 $CaTiO_3$	1400	12.5	–5	3000	Mg_2TiO_4, Mg_2SiO_4, $CaTiO_3$

temperatures (<1400°C), high temperature stability of properties (owing to the effective thermocompensation upon the introduction of small $CaTiO_3$ additions), and low dielectric losses. They are potentially attractive for various electronic applications.

CONCLUSIONS

We studied chemical interactions of Mg_2SiO_4 with Mg_2TiO_4 and $MgTiO_3$ and identified conditions under which the $MgTi_2O_5$ phase (having an adverse effect on microwave losses) is formed in the $MgO–TiO_2–SiO_2$ system. Our results demonstrate that $CaTiO_3$ 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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