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High-Q Microwave Dielectric Materials Based on the Spinel Mg_2TiO_4

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Composite ceramics based on the spinel Mg_2TiO_4 were prepared by a conventional mixed-oxide route. To achieve the temperature stabilization of the dielectric constant, each of the composites was added with 7 mol% $CaTiO_3$. The effect of the substitution of isovalent Co for Mg on the microstructure and the microwave dielectric properties of the composite ceramics was also investigated. A maximum $Q \times f$ value of around 150–160 THz was obtained for the undoped Mg_2TiO_4, whereas a reduced $Q \times f$ value was observed for an increase in the Co concentration in the system $(1-x)Mg_2TiO_4-xCo_2TiO_4$. Upon doping with 7 mol% $CaTiO_3$, the $Q \times f$ value passed through a maximum with increasing Co concentration. Adding ZnO–B_2O_3 to the composite system based on Co-doped Mg_2TiO_4 resulted in a reduction of the sintering temperature by 150°–200°C without any significant degradation in the $Q \times f$ value.

I. Introduction

In the development of modern communication devices such as filters and oscillators, materials with a low dielectric loss (high quality factor $Q = 1/\tan\,\delta$) in the microwave (MW) range are used. The use of high-Q dielectrics as passive MW components—dielectric resonators, dielectric substrates, waveguides, and antennas—makes possible a significant improvement in the performance of communications equipment,[1–3] in particular, better sensitivity and selectivity. This is particularly relevant with the current tendency to expand the operating frequency ranges of MW wireless communications, for instance, up to 20–30 GHz in VSAT, 26–38 GHz in PtP Radiolinks, or 28–40 GHz in LMDS, and applications at frequencies as high as 60 GHz have also been reported. A variety of microwave dielectric components are used in equipment like Low-noise Block (LNB), Block-Up-Converter (BUC) for LMDS, or VSAT terminals. In this case, in addition to the high-quality factor of a material, its price becomes an important factor. Therefore, for the above applications, new, low-cost dielectric materials with a dielectric constant of 10–20 and extremely low dielectric losses are urgently required.

Recently, the intense development of high-Q MW materials based on low-cost raw oxides from the MgO–TiO_2 system has begun.[4–7] In this binary system, two magnesium titanates, which are good candidates for use in MW dielectrics, are known: Mg_2TiO_4 and $MgTiO_3$. Polycrystalline materials based on Mg_2TiO_4 and $MgTiO_3$ are characterized by the dielectric constants $\varepsilon = 14$ and 16, respectively, a negative coefficient of the resonant frequency ($\tau_{f=} -40$–50 ppm/°C), and a low dielectric loss (high Q), whose magnitude reaches $Q = 20\,000$ at 10 GHz for $MgTiO_3$.[6] For the temperature compensation of the negative values of the τ_f of $MgTiO_3$, a small amount of the paraelectric phase Sr(Ca)TiO_3, characterized by a high, positive τ_f, is generally introduced into the main composition.[3–9] It should be noted that, in contrast to undoped $MgTiO_3$, the composite materials based on $MgTiO_3$ always display much lower Q values ($Q = 5000$–7000 at 10 GHz), which can be ascribed to the presence of low-Q Sr(Ca)TiO_3, as well as to the formation of undesirable crystal phases like $MgTi_2O_5$.[5–7] When partially substituting magnesium with cobalt in $MgTiO_3$, materials with high MW parameters have recently been obtained.[4] For instance, in the system $(1-x)Mg_{0.95}Co_{0.05}TiO_3$–$x$$CaTiO_3$, the materials with $\varepsilon \approx 20.3$, $Q \times f \approx 107\,000$ GHz at 7 GHz, and $\tau_f \approx -22.8$ ppm/°C were produced at $x = 0.05$.[4] Moreover, the possibility of using materials based on $MgTiO_3$ in the low-temperature cofired ceramic (LTCC) technique has been reported.[1–9] However, the available literature contains no data regarding the synthesis and properties of MW dielectric materials based on Mg_2TiO_4.

Therefore, the objective of this study was to investigate the formation, phase composition, microstructure, and the MW dielectric properties of composite materials based on the system Mg_2TiO_4–$CaTiO_3$, to study the effect of the partial Co substitution for Mg in this system on the structure and the properties of sintered ceramics, as well as to evaluate the possibility of using these materials in LTCC technology when the ceramics are doped with the glass-forming additives ZnO–B_2O_3.

II. Experimental Procedure

The samples involved in this study were synthesized by the solid-state reaction technique using high-purity MgO, TiO_2, $CaCO_3$, $CoCO_3$, ZnO, and B_2O_3. All the raw reagents were first dried. As MgO is hygroscopic, it was additionally fired at 700°C to avoid any water and CO_2 absorption. The synthesis was carried out in two stages: in the first stage, the binary compounds Mg_2TiO_4, Co_2TiO_4, and $CaTiO_3$ were produced. To do this, the raw reagents were weighed in stoichiometric amounts and then mixed in a ball mill in distilled water. After drying at 100°–150°C, the powders were then homogenized. The preliminary heat treatment (calcination) of the powders was carried out in air in alumina crucibles at 900°–1200°C.

In order to obtain the glass-forming dopant ZnO–B_2O_3, the boron oxide B_2O_3 was dried at 150°–200°C. Both the mixing and the milling of the ZnO–B_2O_3 mixture were carried out in acetone, followed by heating at 600°C.

In order to produce polycrystalline samples, at the second stage, the stoichiometric mixtures of the preliminarily synthesized binary compounds were milled and homogenized in vibration mills in distilled water. After drying at 100°–150°C, the powders were then pressed to form green pellets with a diameter of 8–10 mm and a height of 3–4 mm, which were then sintered at 1200°–1500°C for 2–6 h.

The phase composition of the binary compounds in the system MgO–TiO_2–CaO–CoO was studied by means of X-ray

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diffraction (XRD) analysis on a DRON-3M diffractometer (Cu$K\alpha$ radiation; Burevestnik, Russia). The XRD patterns were measured in the appropriate range with a step of $\Delta 2\theta = 0.02°$ and a time of 10 s. Both SiO_2 (standard 2θ) and NIST SRM 1976—Al_2O_3 (certified intensity standard) were used as internal standards. For the XRD analysis, the JCPDS database was used as a reference for determining the peaks.

The study of the effect of the partial isovalent substitution of Co^{2+} for Mg^{2+} in the spinel Mg_2TiO_4 on the phase composition, the microstructure, and the MW dielectric properties was carried out for the following systems: $(1-x)$ Mg_2TiO_4–xCo_2TiO_4; $0.93[(1-x)$ Mg_2TiO_4–$xCo_2TiO_4]-0.07CaTiO_3$, and $[0.93[(1-x)$ Mg_2TiO_4–$xCo_2TiO_4]-0.07CaTiO_3]+5$ wt% ZnB_2O_4.

The microstructures and the phase distributions of the polycrystalline samples were examined by means of scanning electron microscopy (JSM 5800, JEOL, Tokyo, Japan) using energy-dispersive X-ray spectroscopy (EDX) and the LINK software package (ISIS 3000, Oxford Instruments, Bucks, UK). The dielectric characteristics of the materials, ε, Q, and τ_f, at frequencies around 10 GHz were examined using a modified dielectric resonator method on an appropriate disk sample that resided in an isolated waveguide section. The values of the Q factors were additionally measured by means of the cavity-reflection method using an HP 8719C Network Analyzer (50 MHz–13.5 GHz).

III. Results and Discussion

(1) System $(1-x)Mg_2TiO_4$–xCo_2TiO_4

According to the XRD analyses, the sintered 2MgO–TiO_2 and $2CoCO_3$–TiO_2 mixtures were single phase (Figs. 1 and 2). The Co_2TiO_4 phase is formed at a significantly lower temperature (1100°–1150°C) than that of the Mg_2TiO_4 (Fig. 1). When fired at 1150°C, the magnesium mixture had a noticeable amount of intermediate $MgTiO_3$. It should be noted that the overlapping of the strongest lines of MgO with those of Mg_2TiO_4 prevented the identification of the residual magnesium oxide that did not react during the heat treatment.

With an increase in the firing temperature to 1300°–1400°C, the amount of $MgTiO_3$ in the 2MgO–TiO_2 mixture decreased. However, the XRD analysis indicated that single-phase Mg_2TiO_4 is formed at the sintering temperature, i.e., at 1450°C (Fig. 2).

Previous studies on the formation of Mg_2TiO_4 revealed the partial solid solubility of MgO in the Mg_2TiO_4 matrix.[10] According to the results of Petrova *et al.*,[11] this process could be associated with the partial thermal decomposition of Mg_2TiO_4, accompanied by the formation of $MgTiO_3$ in the following way: $Mg_2TiO_4 \rightarrow Mg_{2+2\delta}Ti_{1-\delta}O_4 + MgTiO_3$.

The authors of Petrova *et al.*[11] have reported that the thermal decomposition of Mg_2TiO_4 becomes negligible when the temperature exceeds 1400°C. This results in a single-phase product at 1400°–1500°C, which is consistent with our XRD data.

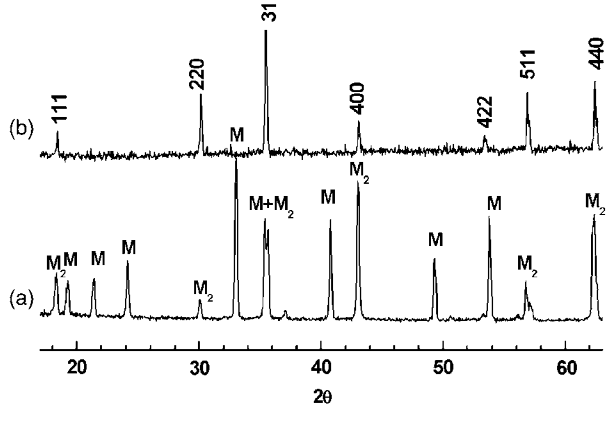

Fig. 1. X-ray diffraction patterns of the mixtures (a) 2MgO–TiO_2 and (b) $2CoCO_3$–TiO_2, after firing at 1150°C for 6 h, M, $MgTiO_3$; M_2, Mg_2TiO_4.

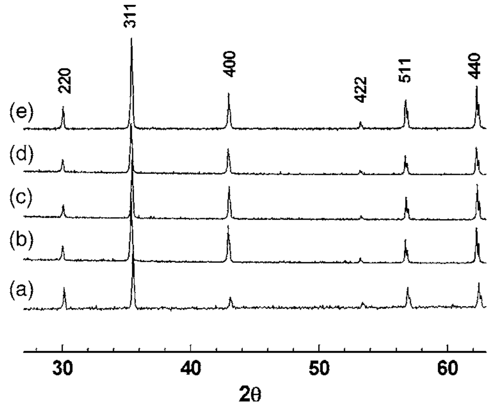

Fig. 2. X-ray diffraction patterns collected on sintered samples of the system $(1-x)Mg_2TiO_4$–xCo_2TiO_4 after firing at 1450°C for 6 h; (a) $x = 1$, (b) $x = 0.02$, (c) $x = 0.05$, (d) $x = 0.1$, (e) $x = 0.2$.

These results were proved by an SEM microstructural analysis of the Mg_2TiO_4 sintered at 1450°C, which revealed no inclusions of secondary phases in the matrix phase (Fig. 3(a)).

XRD studies of the sintered samples of the system $(1-x)$ Mg_2TiO_4–xCo_2TiO_4 show that solid solutions $(Mg_{1-x}Co_x)_2$-TiO_4 with the inverse spinel structure are formed across the entire range of x (Fig. 2). An increase in the cobalt concentration results in only a slight deviation of the parameter a of the unit cell, from 8.43 to 8.44 A, which is within the limits of the measurement accuracy. An SEM investigation of the sintered samples of this system also revealed the absence of secondary phases in the spinel matrix (Fig. 3(b)).

The microwave dielectric properties of the sintered samples demonstrated that the dielectric constant (ε) and the temperature coefficient of resonant frequency (τ_f) are weakly dependent on the cobalt concentration (Table I). However, in contrast to these findings, the magnitude of the quality factor (Q) undergoes a sharp decline at $0<x<0.05$ with increasing cobalt substitution, followed by a smoother decline at higher cobalt contents for $0.05<x$ (Fig. 4(a)).

It should be emphasized that in the case of the stoichiometric nominal composition corresponding to pure Mg_2TiO_4—in spite of the high porosity—the samples demonstrate a $Q \times f$ value as high as 150 000 GHz. To the best of our knowledge, this value is being reported for the first time here for the spinel family, and is comparable with the $Q \times f$ value measured in the $Ba(Mg,Ta)O_3$ perovskites, which are widely recognized high-Q microwave dielectrics. However, it can be clearly seen from Table I that the main drawback of Mg_2TiO_4-based ceramics is the large negative temperature coefficient of resonant frequency (τ_f). This can be overcome by developing composite dielectric materials and introducing phases with a positive temperature coefficient of resonant frequency, for instance, $CaTiO_3$.

(2) System $0.93[(1-x)$ Mg_2TiO_4–$xCo_2TiO_4]-0.07CaTiO_3$

The addition of 7 mol% $CaTiO_3$ to the system $(1-x)$ Mg_2TiO_4–xCo_2TiO_4 resulted in a noticeable lowering of the sintering temperature of the ceramics: from as high as 1420°–1450°C for the undoped system to 1350°–1380°C for the $CaTiO_3$-doped system.

XRD patterns collected on sintered samples of this system differ depending on the cobalt concentration (Fig. 5). In the case of the nominal composition $0.93Mg_2TiO_4$–$0.07CaTiO_3$ ($x = 0$), the ceramics without any cobalt addition were never well sintered, and demonstrated a rather non-homogeneous chemical composition with both sintered and non-sintered interlaced areas. Because of this, at $x = 0$, the samples were not appropriate for either a correct microstructural investigation or for a microwave characterization. According to the consideration presented in Section III (*1*), and taking into account the significantly lower sintering temperature of the samples containing $CaTiO_3$, in the

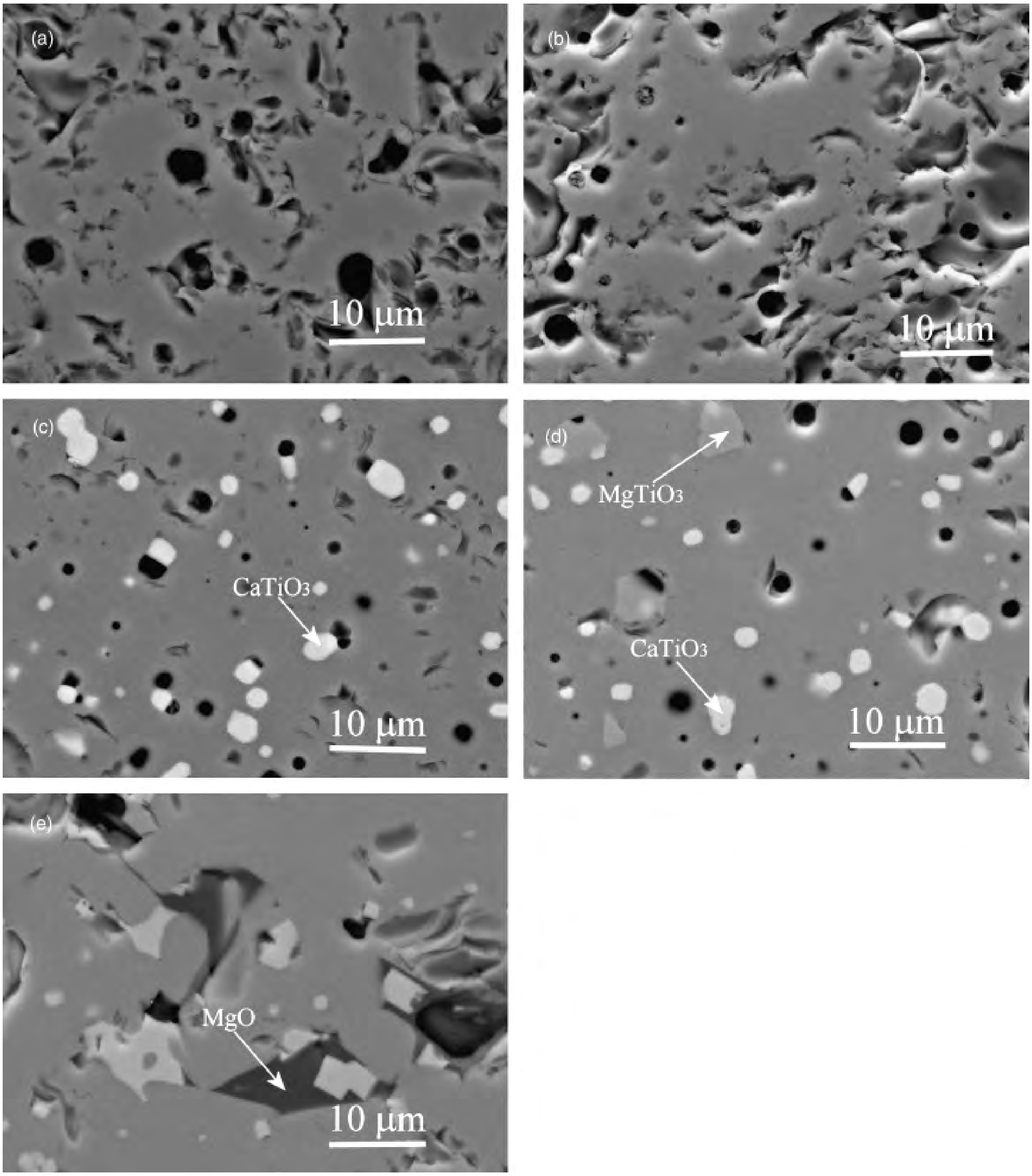

Fig. 3. SEM micrographs from the polished surface of the ceramics with the composition $(1-x)Mg_2TiO_4$–xCo_2TiO_4: (a) $x = 0$ and (b) $x = 0.05$; $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4]$–$0.07CaTiO_3$: (c) $x = 0.02$ and (d) $x = 0.05$; $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4]$–$0.07CaTiO_3$ with 5 wt% ZnO–B_2O_3: (e) $x = 0.02$.

case $x = 0$, one can associate the deteriorated sintering process with the partial thermal decomposition of Mg_2TiO_4. In contrast, the Co substitution for Mg, even at low cobalt concentrations, enhances the sintering of composite ceramics, resulting in the formation of a sufficiently homogeneous microstructure (Fig. 3).

According to the XRD analysis, at low substitution levels corresponding to the ranges $0 < x < 0.04$, the dielectric ceramic contained only two crystal phases: the solid solution $(Mg_{1-x}Co_x)_2TiO_4$ and the perovskite phase $CaTiO_3$ (Fig. 5). This fact has also been confirmed by a detailed microstructural

Table I. Microwave Dielectric Parameters (ε, τ_f, $Q \times f$) Measured at a Frequency 10 GHz for Selected Ceramics Based on the Spinel Mg_2TiO_4

Composition	T_{SINT} (°C)	ε	τ_f (ppm/°C)	$Q \times f$ (THz)
Mg_2TiO_4	1450	14	−50	150
$0.95Mg_2TiO_4$–$0.05Co_2TiO_4$	1420	14	−54	86
$0.80Mg_2TiO_4$–$0.20Co_2TiO_4$	1420	13	−60	75
$0.93Mg_2TiO_4+0.07CaTiO_3$	1420	15	−2	35
$0.93[0.99Mg_2TiO_4$–$0.01Co_2TiO_4]+0.07CaTiO_3$	1400	17	−5	105
$0.93[0.95Mg_2TiO_4$–$0.05Co_2TiO_4]+0.07CaTiO_3$	1400	17	−5	90
$[0.93[0.98Mg_2TiO_4$–$0.02Co_2TiO_4]+0.07CaTiO_3]+5$ wt% ZnO–B_2O_3	1200	16	−8	85

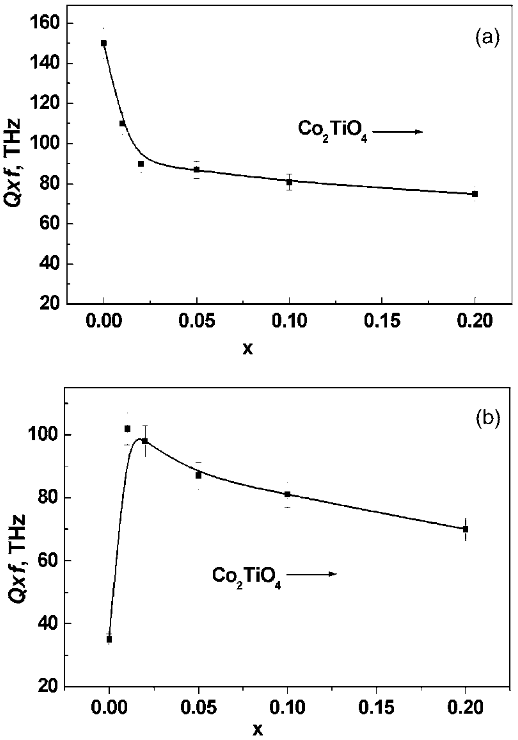

Fig. 4. The product $Q \times f$ as a function of the cobalt content in the systems $(1-x)Mg_2TiO_4$–xCo_2TiO_4 (a), and $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4]-0.07CaTiO_3$ (b).

analysis (Fig. 3). At a higher cobalt concentration ($0.04 \leq x < 1$), in addition to these two main crystal phases, another phase corresponding to the $MgTiO_3$ is formed (Fig. 5). Regardless of the cobalt concentration, the amount of this phase is negligibly small. The presence of residual $MgTiO_3$ is clearly seen on the SEM micrographs, even in the case of very low x ($x = 0.05$). The phase composition of the studied composites, to a large extent, affects their microwave dielectric properties. For instance, in the case $x = 0$, the $Q \times f$ value is as low as just 35 000 GHz, which is associated with the non-homogeneous composition. At the same time, even a slight Co doping ($x = 0.01$) results in a sharp increase in $Q \times f$, which reaches a value as high as 100 000 GHZ (Fig. 4(b)). The highest values of $Q \times f$ of about 90 000–100 000 GHz, were obtained in the case of the two-phase composites corresponding to the ranges $0 < x < 0.04$. A further increase in the cobalt content, which is accompanied by the formation of the additional phase $MgTiO_3$, results in an almost linear decrease in the $Q \times f$ value (Fig. 4(b)). It should be noted that all of the composite materials of the system $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4]-0.07CaTiO_3$ demonstrate a good temperature coefficient of the resonant frequency within the ranges of −5 to −10 ppm/°C (Table I).

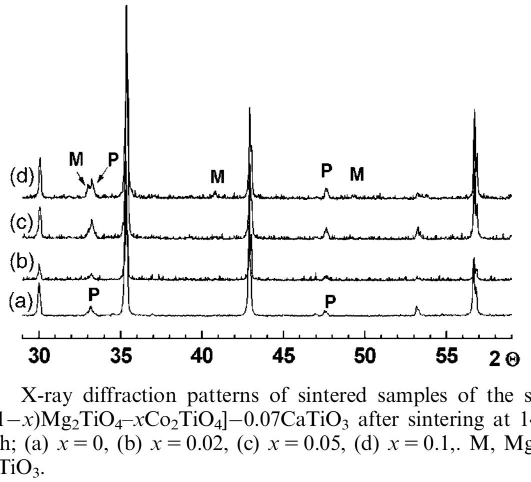

Fig. 5. X-ray diffraction patterns of sintered samples of the system $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4]-0.07CaTiO_3$ after sintering at 1450°C for 6 h; (a) $x = 0$, (b) $x = 0.02$, (c) $x = 0.05$, (d) $x = 0.1$,. M, $MgTiO_3$; P, $CaTiO_3$.

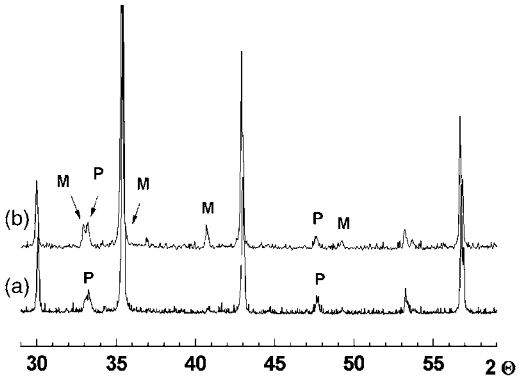

Fig. 6. X-ray diffraction patterns collected from polycrystalline samples with the composition $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4]-0.07CaTiO_3$ which additionally contained 5 wt% of preliminary synthesized ZnB_2O_4 (ZnO–B_2O_3): (a) $x = 0.01$ and (b) $x = 0.05$; M, $MgTiO_3$; P, $CaTiO_3$.

(3) Addition of ZnO–B_2O_3

When 5 wt% of the preliminarily synthesized ZnB_2O_4 (ZnO–B_2O_3) was added to the system $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4]-0.07CaTiO_3$, the sintering temperature decreased by 150°–200°C: in this case, well-sintered ceramics were formed at 1200°–1250°C. According to the XRD data the introduction of the dopant ZnO–B_2O_3 did not result in drastic changes in the phase composition of the polycrystalline materials. In the case of a low substitution ($0 \leq x \leq 0.04$), the sintered composites contain only two crystal phases: spinel-like solid solutions based on Mg_2TiO_4 as well as the perovskite $CaTiO_3$ (Fig. 6, pattern a). An increase in the cobalt concentration over $0.04 \leq x$ resulted in the formation of a secondary phase $MgTiO_3$, which was also observed in the undoped materials (Fig. 6, pattern b).

SEM microstructural analyses of the sintered samples containing a nominal 5 wt% ZnO–B_2O_3, in contrast to the undoped materials, even at a low cobalt concentration ($0 \leq x \leq 0.04$), in addition to two major crystal phases (spinel and perovskite), indicated the presence of a third Mg-rich phase (Fig. 3(e)).

It should be noted that the addition of the dopant ZnO–B_2O_3, which results in a significant (up to 150°–200°C) reduction of the sintering temperature, does not initiate any noticeable degradation in the electrophysical parameters of the sintered material. In particular, the magnitude of $Q \times f$, which in the case of the composition $0.93[0.98Mg_2TiO_4$–$0.02Co_2TiO_4]-0.07CaTiO_3$ is as high as 100 000, decreases by only 15% when 5 wt% ZnO–B_2O_3 is added, and is equal to 85 000 at 10 GHz. A slight decrease in the $Q \times f$ value, observed after the addition of 5 wt% ZnO–B_2O_3, is probably due to the effect of MgO-rich inclusions in the matrix phase. The results indicate the possibility of a further reduction in the sintering temperature to 900°–950°C, which is required for most LTCC applications. This could be attained by a further increase in the concentration of the dopant ZnO–B_2O_3 that is introduced into the basic composition. However, this will most probably lead to a severe degradation in the value of $Q \times f$.

IV. Conclusions

(a) The cubic spinel structure is formed across the entire range of Co concentration in the system $(1-x)Mg_2TiO_4$–xCo_2TiO_4 ($0 < x \leq 1$).

(b) Sintered Mg_2TiO_4 demonstrates a $Q \times f$ value as high as 150–160 THz, even for noticeably porous ceramics, together with a relatively high negative temperature coefficient τ_f.

(c) In the system $(1-x)Mg_2TiO_4$–xCo_2TiO_4, an increase in Co concentration resulted in a reduction of the $Q \times f$ value.

(d) In the system $(1-x)Mg_2TiO_4-xCo_2TiO_4$, containing the $CaTiO_3$ additive, the $Q\times f$ value passed through a maximum with increasing Co concentration.

(e) The introduction of 5 wt% of the dopant $ZnO–B_2O_3$ into the composite ceramics based on Co-doped Mg_2TiO_4 results in a 150°–200°C reduction in the sintering temperature without a significant reduction in the value of $Q\times f$.

(f) Owing to their easy processing and high-quality factor, new composite materials based on the doped spinel Mg_2TiO_4 demonstrate a good potential for use in modern MW engineering.

References

[1] K. Wakino, "High Frequency Dielectrics and Their Applications"; pp. 97–106 in *Proceedings of the 6th IEEE International Symposium on Application of Ferroelectrics*. Institute of Electrical and Electronic Engineers, New York, 1986.

[2] S. J. Fiedziuszko, I. C. Hunter, T. Itoh, Y. Kobayashi, T. Nishikawa, S. N. Stitzer, and K. Wakino, "Dielectric Materials, Devises, and Circuits," *IEEE Trans. Microwave Theory Technol.*, **MTT-50**, 706–20 (2002).

[3] A. G. Belous, "Physicochemical Aspects of the Development of MW Dielectrics, and Their Use," *J. Eur. Ceram. Soc.*, **21**, 2717–22 (2001).

[4] J.-H. Sohn, Y. Inaguma, S.-O. Yoon, M. Itoh, T. Nakamura, S.-J. Yoon, and H.-J. Kim, "Microwave Dielectric Characteristic of Ilmenite-Type Titanates with High-*Q* Values," *Jpn. J. Appl. Phys.*, **33** [9B] 5466–70 (1994).

[5] N. Ichinose and H. Yamamoto, "Effect of Additives on Microwave Dielectric Properties in Low-Temperature Sintering (Mg,Ca)TiO_3 Based Ceramics," *Ferroelectrics*, **201**, 255–62 (1997).

[6] H. Cheng-Liang and P. Chung-Long, "Low-Temperature Sintering and Microwave Dielectric Properties of $(1-x)MgTiO_3–xCaTiO_3$ Ceramics Using Bismuth Addition," *Jpn. J. Appl. Phys.*, **41**, 707–11 (2002).

[7] H. Cheng-Liang, P. Chung-Long, and Y. Cheng-Chi, "Low Firable $0.95MgTiO_3-0.05CaTiO_3$ Microwave Dielectrics," *J. Mater. Sci. Lett.*, **21**, 149–51 (2002).

[8] H. Jantunen, R. Rautioaho, A. Uusimaki, and S. Leppavuori, "Compositions of $MgTiO_3–CaTiO_3$ Ceramic with Two Borosilicate Glasses for LTCC Technology," *J. Eur. Ceram. Soc.*, **20**, 2331–6 (2000).

[9] H. Cheng-Liang and W. Ming-Hung, "Improved High *Q* Value of $MgTiO_3–CaTiO_3$ Microwave Dielectric Ceramics at Low Sintering Temperature," *Mater. Res. Bull.*, **36**, 2741–50 (2001).

[10] G. A. Mikirtcheva, S. A. Petrov, V. I. Shitova, V. I. Petrova, F. S. Novikova, and R. G. Grebenschikov, "Temperaturnoye Poviedenie Dititanata Magniya," "Temperature Behaviour of the Magnesium Dititanate," *Russ. J. Appl. Chem.*, **1** [1] 17–20 (1998).

[11] M. A. Petrova, G. A. Mikirticheva, A. S. Novikova, and V. F. Popova, "Spinel Solid Solutions in the Systems $MgAl_2O_4–ZnAl_2O_4$ and $MgAl_2O_4–Mg_2TiO_4$," *J. Mater. Res.*, **12** [10] 2584–8 (1997). □