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Microwave composite dielectrics based on magnesium titanates

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Abstract

Composite dielectrics comprising the crystal phases of Co-doped magnesium titanates $MgTiO_3$ and Mg_2TiO_4, and $CaTiO_3$ were examined with regard to their phase composition and its effect on the microwave dielectric properties. In the case of $MgTiO_3$-based composites an increase in the Co concentration results in increasing amount of an additional phase $MgTi_2O_5$, which significantly deteriorates the product $Q \times f$. In contrast, the materials based on the spinel Mg_2TiO_4 never contain $MgTi_2O_5$, and consequently demonstrate excellent $Q \times f$ magnitude which is as high as 100,000 GHz at low Co doping. At higher Co concentration, however, an additional phase $MgTiO_3$ appears in these materials that is accompanied by a slight reduction of the $Q \times f$ magnitude. A slight addition (5 wt.%) of the glass-forming zinc borate into the Mg_2TiO_4-based composite allows a noticeable reduction of its sintering temperature by 150–200 °C without a significant degradation of its dielectric properties.

Keywords: Sintering; Composites; Dielectric properties; Magnesium titanates; Functional applications

1. Introduction

With the current tendency of increasing operating frequencies of the MW wireless communications new low-cost dielectric materials with extremely low dielectric loss in the microwave (MW) range (high electrical quality $Q = 1/tg\delta$) and dielectric constant of 10–20 are urgently required to provide high selectivity of MW devices.[1] These materials can be based on binary magnesium titanates ($MgTiO_3$ and Mg_2TiO_4) which since recently are finding a variety of applications in MW engineering.[2] The above compounds have dielectric constant $\varepsilon = 16$ and 14 correspondingly, the negative coefficient of the resonant frequency ($\tau_f = -40$–50 ppm/C), and low dielectric loss—high Q, the magnitude of which reaches $Q = 20{,}000$ at 10 GHz for $MgTiO_3$.[2,3] The temperature compensation of the negative values of τ_f in $MgTiO_3$ and Mg_2TiO_4 can be attained by an addition of the crystal phase with the positive τ_f into the material.[3–5] The perovskite $CaTiO_3$ with $\varepsilon = 160$ and high positive τ_f is often used as the additional phase in the $MgTiO_3$ matrix. However, currently available composite MW dielectrics based on $MgTiO_3$ demonstrate rather low to moderate product $Q \times f$ because of the formation of undesirable low-Q crystal phases.[3–5] Recently, the cobalt substitution for magnesium in $MgTiO_3$ has been shown to improve the MW parameters of composites.[2,5] Moreover, a possibility to use the materials based on $MgTiO_3$ in the LTCC technique has been reported.[6] However, the available literature contains no sufficient data regarding the properties of temperature compensated MW dielectrics based on Co-substituted magnesium titanates $MgTiO_3$ and Mg_2TiO_4.

Therefore, this study focused on the investigation of the correlation between the phase composition, microstructure, and MW dielectric properties of the composite materials based on the systems $(Mg_{1-x}Co_x)TiO_3$–$CaTiO_3$ and $(Mg_{1-x}Co_x)_2TiO_4$–$CaTiO_3$, as well as the evaluation of their potential for the applications in LTCC technology.

2. Experimental procedure

The ceramics based on the systems $(Mg_{1-x}Co_x)TiO_3$–$CaTiO_3$ and $(Mg_{1-x}Co_x)_2TiO_4$–$CaTiO_3$ were produced by the conventional mixed oxide route. The starting reagents were pure MgO, TiO_2, Co_3O_4, and $CaCO_3$ (99.9%). The phase composition and crystal lattice parameters of sintered ceramics were examined by means of X-ray diffraction analysis (XRD) on the diffractometer DRON—3M (Cu Kα radiation). Microstructural analysis of the ceramic samples was performed by means of scanning electron microscopy (JEOL, JSM 5800, Tokyo, Japan)

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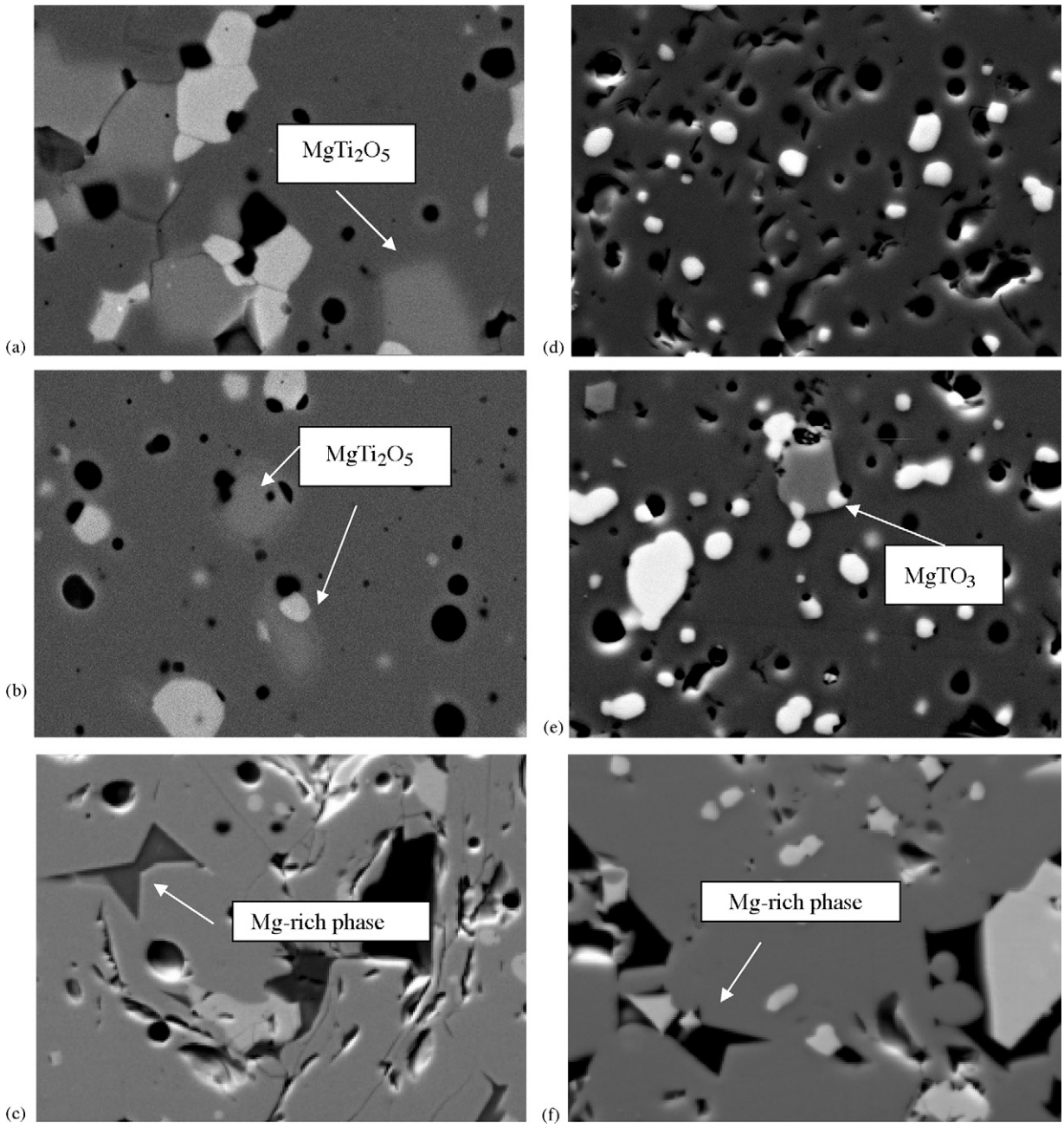

Fig. 1. Typical SEM micrographs of the systems (a–c) $[(1-x)\ MgTiO_3–xCoTiO_3]-0.07CaTiO_3$ and (e and f) $[(1-x)\ Mg_2TiO_4–xCo_2TiO_4]-0.07CaTiO_3$ for $x = 0.01$ (a and d), $x = 0.05$ (b, c, e and f). The microphotographs (e and f) represent the samples with 5 wt.% $ZnO–B_2O_3$.

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 8–10 GHz were examined using a cavity reflection method on the Network Analyser PNA-L Agilent N5230A.

3. Results and discussion

3.1. System [(1 − x) MgTiO3–xCoTiO3] − 0.07CaTiO3

XRD studies of the sintered samples of the system $[(1-x)\ MgTiO_3–xCoTiO_3]-0.07CaTiO_3$ show that the expected two-phase composition is never formed: in addition to the main phases of ilmenite $MgTiO_3$ and perovskite $CaTiO_3$ the ceramics always contain a small amount of the third phase corresponding to $MgTi_2O_5$. These results are confirmed also by the electron microscopy (Fig. 1a–c). EDS microanalysis evidences that Co is introduced into the ilmenite crystal lattice, its amount into the matrix phase increases with increasing x. Similarly, a slight amount of Co has been revealed also in the third phase $MgTi_2O_5$. However, no cobalt was present inside the inclusions of $CaTiO_3$. It should be noted that the amount of an additional phase $MgTi_2O_5$ in studied composites is not anyhow affected by the changes in the Co-concentration (Fig. 1a and b). Therefore,

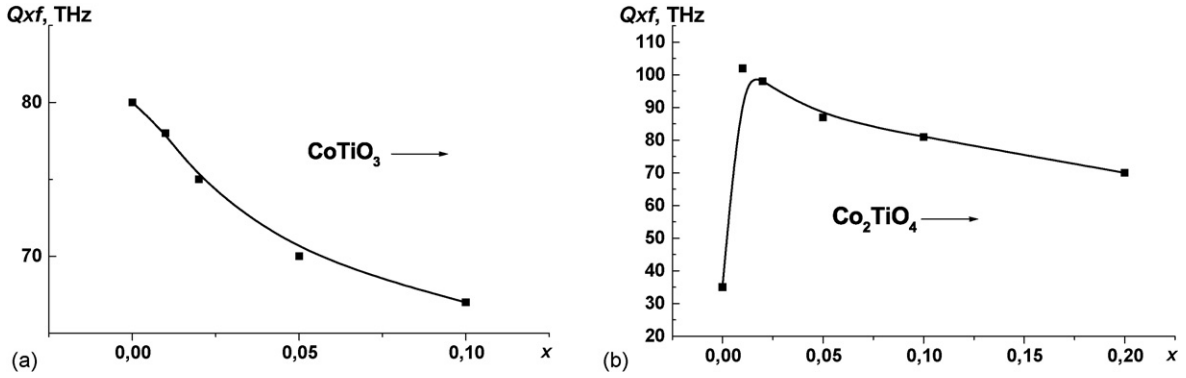

Fig. 2. The product $Q \times f$ of the systems (a) $[(1-x)\ MgTiO_3$–$xCoTiO_3] - 0.07CaTiO_3$ and (b) $[(1-x)\ Mg_2TiO_4$–$xCo_2TiO_4] - 0.07CaTiO_3$ as a function of x. The samples were sintered for 6 h at 1350 °C (a) and 1400 °C (b).

the presence of an additional $MgTi_2O_5$ may not be probably connected with the presence of Co, and derives from the formation mechanism established elsewhere for $MgTiO_3$.[7] Even after the prolonged soaking at sintering temperature for 6–10 h the amount of $MgTi_2O_5$ in the matrix was not suppressed, and no one can expect that any further improvement in the phase equilibrium may be attained. As a consequence of the presence of $MgTi_2O_5$ the magnitude of the product $Q \times f$ of studied composites never reaches high values of a "pure" $MgTiO_3$. It is almost unaffected by the changes in Co-concentration being in the range of $Q \times f = 70{,}000$–$80{,}000$ GHz (Fig. 2a). The magnitude of dielectric constant (ε) slightly increases with Co concentration probably due to an increase in the ionic radius, and varies within the range of $\varepsilon = 20$–21. It should be also noted that an addition of 7 mol% of $CaTiO_3$ resulted in the effective temperature stabilization of temperature coefficient τ_f which was within the ranges of $\tau_f = -7$ to 1 ppm/C (Table 1). When 5 wt.% of the mixture $ZnO \times B_2O_3$ was added into the basic composition the ceramics was successfully sintered at 1100 °C. Microstructural analysis of the ceramics which contain 5% zinc borate denote the presence of new Mg-reach phase in addition to the phase combination established for $MgTiO_3$-composite (Fig. 1c). The presence of this phase was probably responsible for the further reduction of the product $Q \times f$ down to $Q \times f = 40{,}000$–$50{,}000$ GHz (Table 1). The dielectric constant of these ceramics was in the range of $\varepsilon = 20$–21.

3.2. System $[(1-x)\ Mg_2TiO_4$–$xCo_2TiO_4] - 0.07CaTiO_3$

In contrast to the findings reported for the Co-doped ilmenite $MgTiO_3$ when Co substitutes for Mg in the spinels Mg_2TiO_4 a decrease in the $Q \times f$ magnitude is observed (Fig. 2a). At $0 < x < 0.05$ the magnitude of quality factor (Q) undergoes a sharp drop with increasing cobalt substitution followed then by a smoother fall at higher cobalt content for $0.05 < x$ (Fig. 2 a). At the same time both the dielectric constant (ε) and the temperature coefficient of resonant frequency (τ_f) demonstrate rather weak dependence on the cobalt concentration (Table 1).

It should be emphasized that in the case of stoichiometric nominal composition corresponding to pure Mg_2TiO_4 – in spite of the high porosity – the samples demonstrate the product $Q \times f$ as high as 160,000 GHz. According to the best of the authors' knowledge, this value is for the first time reported here for the spinel family, and it is comparable enough with the product $Q \times f$ measured in the $Ba(Mg,Ta)O_3$ perovskites, which are widely recognized representatives of high-Q microwave dielectrics.

The addition of 7 mol% $CaTiO_3$ into the compounds $(1-x)$ Mg_2TiO_4–xCo_2TiO_4 always results in a noticeable lowering the sintering temperature of the ceramics which is as high as 1420–1450 °C for the "pure" spinels, whereas it drops down to 1350–1380 °C with the $CaTiO_3$. However, in the case of undoped spinels $0.93Mg_2TiO_4$–$0.07CaTiO_3$ ($x = 0$) an addition of 7 mol% $CaTiO_3$ never resulted in the well sin-

Table 1
The phase composition and microwave dielectric properties of sintered materials of the systems (a) $[(1-x)\ MgTiO_3$–$xCoTiO_3] - 0.07CaTiO_3$ and (b) $[(1-x)$ Mg_2TiO_4–$xCo_2TiO_4] - 0.07\ CaTiO_3$

Nominal composition	T_{SINT} (°C)	Phase composition	ε	$Q \times f$ (GHz)
$MgTiO_3$*	1450	$MgTiO_3$	16	200,000
$0.93MgTiO_3$–$0.07CaTiO_3$	1400	$MgTiO_3$, $CaTiO_3$	20	80,000
$0.93Mg_{0.98}Co_{0.02}TiO_3$–$0.07CaTiO_3$	1350	$MgTiO_3$, $CaTiO_3$, $MgTi_2O_5$	21	77,000
$0.93Mg_{0.95}Co_{0.05}TiO_3$–$0.07CaTiO_3$	1350	$MgTiO_3$, $CaTiO_3$, $MgTi_2O_5$	21.5	65,000
$(0.93Mg_{0.95}Co_{0.05}TiO_3$–$0.07CaTiO_3) + 5$ wt.% ZnO–B_2O_3	1100	$MgTiO_3$, $CaTiO_3$, $MgTi_2O_5$, MgO-reach phase	21.0	45,000
Mg_2TiO_4	1500	Mg_2TiO_4	14.2	160,000
$0.93Mg_2TiO_4$–$0.07CaTiO_3$	1450	Mg_2TiO_4, $MgTiO_3$, $CaTiO_3$	13.5	30,000
$0.93(Mg_{0.98}Co_{0.02})_2TiO_4$–$0.07CaTiO_3$	1400	Mg_2TiO_4, $CaTiO_3$	13.0	105,000
$0.93(Mg_{0.95}Co_{0.02})_2\ TiO_4$–$0.07CaTiO_3$	1400	Mg_2TiO_4, $CaTiO_3$, $MgTiO_3$	19.2	90,000
$0.93(Mg_{0.98}Co_{0.02})_2\ TiO_4$–$0.07CaTiO_3 + 5$ wt.% ZnO–B_2O_3	1200	Mg_2TiO_4, $CaTiO_3$, MgO-reach phase	18.6	80,000

* The data from the Ref. 2.

tered ceramics, which demonstrated rather non-homogeneous chemical composition with both sintered and non-sintered interlaced areas. This could be probably associated with the partial thermal decomposition of Mg_2TiO_4 which may pass via the scheme $Mg_2TiO_4 \rightarrow Mg_{2+2\delta}Ti_{1-\delta}O_4 + MgTiO_3$, and which may be observed around sintering temperature.[8]

In contrast, the Co substitution for Mg even at low cobalt concentrations enhances sintering of the composite ceramics resulting in the formation of enough homogeneous microstructure (Fig. 1d). According to both XRD and SEM analysis at low substitution degree ($0 < x < 0.04$) the ceramics contain only two crystal phases: solid solutions $(Mg_{1-x}Co_x)_2TiO_4$ and the perovskite phase $CaTiO_3$ (Fig. 1d). At higher cobalt concentration ($0.04 \leq x < 1$) in addition to these two main crystal phases another phase corresponding to $MgTiO_3$ is formed (Fig. 1e). Regardless of the cobalt concentration, the amount of this phase is negligibly small. The phase composition of studied composites to a large extent affects their microwave dielectric properties. For instance, in the case $x = 0$ the product $Q \times f$ is as low as only 35,000 GHz that is associated with the non-homogeneous composition. At the same time even a slight Co doping ($x = 0.01$–0.04) results in a sharp increase in the $Q \times f$ which reaches the magnitude as high as 100,000 GHz (Fig. 2b). The further increase in the cobalt content ($0.04 \leq x$), which is accompanied by the formation of $MgTiO_3$, results in the almost linear decrease in the $Q \times f$ product (Fig. 2b). It should be noted that all of the materials of the system $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4] - 0.07CaTiO_3$ demonstrate good temperature coefficient of the resonant frequency within the ranges of -5 to -10 ppm/C.

When adding 5 wt.% preliminary synthesized ZnB_2O_4 (ZnO–B_2O_3) into the compounds of the system $0.93[(1-x)Mg_2TiO_4$–$xCo_2TiO_4] - 0.07CaTiO_3$ the sintering temperature decreases by 150–200 °C: in this case well sintered ceramics is formed at 1200–1250 °C. SEM microstructural analysis of the samples containing 5 wt.% ZnO–B_2O_3, in contrast to the undoped materials, denotes the presence of another third Mg-rich phase in addition to two major crystal phases (spinel and perovskite) even at low cobalt concentration ($0 \leq x \leq 0.04$) (Fig. 1f). The presence of this phase, similarly like in the $MgTiO_3$-based materials, results in a slight reduction of the product $Q \times f$, from the values around 100,000 GHz in the case of the composition $0.93[(0.98 Mg_2TiO_4$–$0.02Co_2TiO_4] - 0.07CaTiO_3$ to 80,000 GHz for the same composition containing 5 wt.% zinc borate. Though the sintering temperature of sintered composites was still high enough for the LTCC applications one can nevertheless expect its further efficient reduction with increasing content of the zinc borate.

4. Conclusions

The magnitude of microwave quality factor of the composite dielectrics based on magnesium titanates $MgTiO_3$ and Mg_2TiO_4 is to a large extent effected by the phase composition of the ceramics. The composites based on the ilmenite $MgTiO_3$ always tend to form an additional phase $MgTi_2O_5$ which deteriorates dielectric properties significantly. In contrast, the ceramics based on Mg_2TiO_4 in which the phase $MgTi_2O_5$ is not represented, demonstrate the magnitude of the $Q \times f$ product as high as 100,000 GHz, which undergoes only weak reduction when zinc borate is added.

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